

FINAL REPORT

REVIEW AND EVALUATION OF
PAST SOLAR-CELL DEVELOPMENT EFFORTS

JUNE 1968

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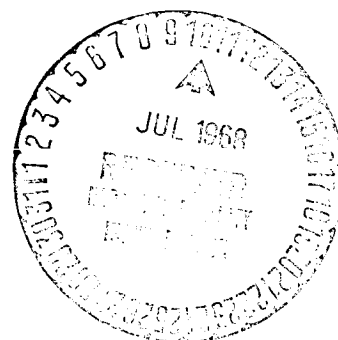
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Astro-Electronics
Division

Princeton, New Jersey

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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FINAL REPORT

REVIEW AND EVALUATION OF PAST SOLAR-CELL DEVELOPMENT EFFORTS

by

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JUNE 1968

PREPARED UNDER CONTRACT NO. NASW-1427

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PREFACE

This is the final report on the "Review and evaluation of past solar cell development efforts". This work was performed by members of the Physical Research Laboratory (M. Wolf, Manager) of the Astro-Electronics Division of RCA, Princeton, New Jersey, for the National Aeronautics and Space Administration, under Contract Number NASW-1427. The period of performance for this program was June 1, 1966, through May 31, 1968. Mr. M. Wolf was the Project Director, and Dr. P. A. Crossley was the Project Scientist. Others who participated in the work were G. T. Noel and K. Brodtman.

The effort on this contract was directed by Mr. Arvin H. Smith, Chief, Solar and Chemical Power Systems, Office of Advanced Research and Technology, NASA Headquarters, Washington, D.C.

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The literature search involved a number of foreign language publications for which translations were necessary. For elucidating historical papers in German, thanks are due to Mr. M. Byczkowski and Mrs. S. Winkler, and for translations and interpretive help with modern Russian papers, our thanks go to Prof. J. J. Loferski.

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ABSTRACT

This report provides a historical account of all research done on the photovoltaic effect, and on devices which use this effect for power conversion. This account is used as the basis for a critical analysis and evaluation of the past research in this field, which was aimed at providing solar photovoltaic conversion devices for generating power in space. From this examination of past work, suggestions are derived for research into specific areas with reasonably high potential for yielding results which will provide improved devices for future application in space power systems. This report also contains an extensive bibliography listing the scientific publications, conference reports, and government contract reports which have been found relevant in this work.

SUMMARY

The objective of this program has been to identify those areas of research and development in the photovoltaic field where it appears probable that results will be achieved that will be pertinent to solving present and foreseeable problems arising in the application of solar photovoltaic devices to the generation of electrical power in space. To achieve this objective, all of the published papers, conference papers, and research contract reports that could be traced and obtained in the subject field and in closely related fields were read. From this work a historical account of research and development pertaining to solar cells has been written. Specific areas of this research have been critically analyzed and evaluated, and the results of this examination have been used to derive recommendations for future work. Major areas in which suggestions for future research are made, include p-n junction and recombination theory, thin silicon cells, drift-field cells, CdS and CdTe thin-film cells, lithium-doped silicon cells, and shallow-junction silicon cells. Accounts of the activity in these areas form the major part of this report. In addition, two contributions to cell theory are given in detail in the Appendices, and a list of the scientific papers and government research contract reports which were used in this work are given in the Bibliography.

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I. OBJECTIVES AND METHODS

I. OBJECTIVES AND METHODS

A. OBJECTIVES

Devices using the photovoltaic effect have for the past decade provided the only viable electrical power source for space vehicles with a lifetime exceeding a few weeks. The construction of arrays of these devices to convert sunlight into useful power at a level of up to about 1 kW is now a mature engineering field. It was believed until recently that other power sources would become available for long-duration missions during the late 1960's, and, in particular, that they would be used when the art of propulsion had advanced sufficiently to launch payloads requiring kilowatts of power. These alternative power sources were thought to use solar or radio-isotope heat in turbine, thermoelectric, thermionic, or thermophotovoltaic conversion systems.

Large research efforts in these areas have produced remarkable advances, but these systems are not yet sufficiently developed for use in high-power systems, nor do their lower power varieties yet provide cost-effective systems in competition with solar photovoltaic systems for most cases of application. Although there is little doubt that these new devices will eventually be successfully applied in large power systems, it has become generally recognized that solar photovoltaic systems capable of supplying up to 50 kW of power will provide very competitive systems, both from the technical and cost view-points.

For these reasons, much research on the photovoltaic effect and on devices for its application has been supported under the US space effort, and it appears necessary that such research be continued in the future. To enable the research effort to be deployed in the areas most likely to produce needed results, the work under this contract has been performed. The objective has been to recommend a number of specific areas where research is most likely to yield improved devices, and to present the evidence on which these recommendations are based.

B. METHODS

1. Literature Search

The starting point for the work of this contract has been a literature search. This has been made as comprehensive as possible, and has covered (i) material published in the scientific literature from the time of Becquerel's discovery of the photovoltaic effect in 1839 to the present time, (ii) papers presented at scientific conferences, and (iii) reports on research funded by the US government. The subject field has encompassed the photovoltaic effect and devices employing it, but has not included

any of the development work related to array fabrication or deployment methods. Although the subject of radiation damage has been covered, the total amount of research which has been done in this field is much larger than that needed for the purposes of the present work, so that no attempt has been made to provide complete coverage of this literature.

Searching the published scientific literature is of course comparatively simple, and no special difficulties have been encountered. Obtaining transcripts of papers presented at scientific conferences has not been so easy, and it has been necessary to rely almost wholly on direct approaches to well-known workers in the field. Consequently, it is expected that the degree of coverage obtained for this material is relatively low. However, such papers can be regarded as supplemental to published works, so that this is not a source for concern. Reports on government-sponsored research have also proved difficult to obtain in some instances. The problem here has been to learn of relevant research projects, and to identify the reports generated under them. Once this hurdle has been passed, it has generally been found comparatively easy to obtain the needed copies from the documentation centers operated by DoD and NASA. Aside from personal knowledge, the most useful source of information on relevant research projects has been the PIC Briefs issued by the Interagency Power Information Center. Although this source appears to be relatively complete for contracts issued since about 1964, the coverage during the period 1960-1964 is noticeably incomplete, and the Briefs do not cover the pre-1960 period. Although many reports have been obtained on projects not mentioned in the PIC Briefs, it is felt that a proportion of the research during the period 1955-1960 must have gone unexamined for this reason. It seems highly improbable that any major developments from this period were not eventually reported in the published literature or incorporated in later devices or approaches, and have consequently not been accounted for, but it has been a disappointment to feel that the coverage in this area may have been less than complete. It should also be mentioned that the lack of report identification numbers in the PIC Briefs has proved particularly irksome. Ideally, the Briefs would provide the accession numbers allocated by the DoD and NASA documentation facilities. Whereas the necessary liaison would probably be difficult to achieve, and would also delay issuance of the Briefs, it would appear possible to provide the report number as issued by the contracting agency. This would greatly facilitate obtaining needed reports. Finally, it must be recorded that a notable omission from many reports is an indication of the period of time during which the reported work was done, and of the personnel involved. The responsibility for this ultimately rests with the contractor, and it is urged that these be included as a matter of course in all reports, since they are almost essential to allow correlation between reports and scientific papers published on the results of the same work.

The papers and reports which were collected during the literature search are listed in the bibliography at the end of this report. Every one of the 596 papers and 204 reports was read completely, and an abstract prepared. These abstracts were filed under an indexing system so that papers relevant to a given topic could be located quickly.

2. Historical Review

From the material assembled during the documentation phase, a historical review was written covering the entire photovoltaic research effort from 1839 to the present. This review occupies the greater part of this report, the material from earlier reports being reprinted to provide a unified and complete account. This review also contains, to a large degree, an evaluation of the work done in the past, since it contains comparisons with later work and interpretations in terms of present-day concepts. However, care has been taken to give a factual account and to insert conclusions only where it is believed that the evidence available indicates that there will be no disagreement with the conclusions. In cases more open to varying interpretations, all sides of the subject under discussion have been presented in the historical review, and further discussion reserved to the analysis and evaluation chapters. In this way, it is hoped that separation between established fact and editorial opinion has been maintained in this report.

3. Evaluation and Analysis

As mentioned above, a considerable amount of evaluation and analysis was performed in assembling a historical account of photovoltaic research. In the chapters of this report following the historical review, further evaluation and analysis is reported. This discussion has been limited to areas where it is believed that more detailed consideration is worthwhile, bearing in mind the objectives of the project in hand. In these evaluation and analysis phases, an effort has been made to provide critical but objective comparisons and comments. While it will no doubt have been impossible to avoid offending someone, the attempt has been made to avoid being partisan in criticizing the results of others, and to provide as fair an account as possible.

4. Suggestions

Based on the results of the preceding phases, recommendations have been made for research in specific areas. These suggestions have been made selectively, since it is assumed that infinite funding for photovoltaic research is not available. In addition, past experience has indicated that small research efforts are rarely worthwhile, and it appears that a better return on investment in research is obtained from large efforts in limited areas than from many small efforts over a wide range of topics. It is believed that the photovoltaic field has now sufficiently matured that research efforts can be accurately directed into limited areas likely to yield useful results. This is in many ways a basic premise of this project.

A final word of caution should be inserted at this point, however. An analysis of this type operates largely by logical processes, by extrapolation from past research results. While thorough knowledge of a given field and of the past accomplishments within it and neighboring fields is a necessary basis for such logical extrapolation processes, it can also provide an intuitive "feel" for the subject which has occasionally

been used to supplement logical justification for pursuing a particular research topic. This, however, still provides no means for identifying areas of research where entirely unexpected results will be obtained. Such a statement is of course tautologous, but it serves to indicate a limitation on the results which can be obtained by logic from limited starting data. Such a noticeable example of unexpected and useful results exists in the photovoltaic field, in the form of the CdS cell. This example provides plenty of substance for not losing sight of this limitation on the present analysis and the resultant recommendations.

5. Organization of this Report

This report provides a historical account of all research and development work done on photovoltaic devices, followed by an evaluation and analysis of this past research. Finally, suggestions for future research areas are discussed.

The historical account is given in the first three chapters (II through IV), with the period being divided into the earliest work (1839-1940), the development of practical energy conversion devices (1940-1955), and the refinement of the devices during the most recent period (1955-present). Within each chapter, the material is divided into subject areas, generally by device type, and the account is chronological within the subject area.

In chapter V, the research and development done in the past is evaluated and analyzed, attention being concentrated on those areas where discussion is pertinent to the foreseeable problems arising in space power generation. In this chapter, the material is organized parallel to that presented in chapter IV, to provide easy correlation between the analysis in chapter V and the factual account of the research in chapter IV.

Based on the conclusions of chapter V, suggestions for future research areas most likely to yield fruitful results are presented in chapter VI. Here, the organization of the material has been different from that used in preceding chapters, the subject areas being approaches to a common problem (e.g., efficiency improvement, cost reduction, etc.), to stress the fact that the achievement of these objectives is the motivation for the suggested further work.

Appendices I and II describe two contributions to cell theory, which have been made during the course of this work. Appendix III provides chronological charts describing Government-funded research projects, to aid the reader in keeping track of the various programs which are discussed in the main body of the report.

The bibliography provides a listing of publications and reports which have been found to be useful during the course of this work.

II. DISCOVERY OF THE PHOTOVOLTAIC EFFECT AND EARLY WORK

GLOSSARY OF SYMBOLS FOR SECTION II

$[A]$	chemical activity
B	constant
C	constant
C_1, C_2	constants proportional to electron density in unilluminated semiconductor
d	junction width
E_{\max}	maximum energy of a photo-emitted electron
h	Planck's constant
J	illumination intensity or current density, in context
J_L	light-generated current density
J_0	reverse saturation current density
k	Boltzmann's constant
k_2, k_3	constants
N	electron concentration or carrier concentration in unilluminated region, in context
N_0	carrier concentration in illuminated region
n	electron concentration
q	electronic charge
T	absolute temperature
V	potential difference
V_0	dark emf or barrier height, in context
V_{oc}	open-circuit voltage
W	barrier height
X	constant related to carrier mobilities
α	constant
β	constant
μ_n	electron mobility
μ_p	hole mobility
ν	frequency
ρ_{∞}	limiting reverse resistance
Φ	Donner potential difference

II. DISCOVERY OF THE PHOTOVOLTAIC EFFECT AND EARLY WORK

A. INTRODUCTION

This chapter is an account covering the first part of the history of research into the photovoltaic effect. The period covered in this part of the history is from the earliest work (1839) to 1940. The next chapter covers the historical development from 1940 to the present day. The dividing point at 1940 has been chosen because it forms a natural break in the development of the subject. During the earlier period, a large body of phenomenological knowledge was built up on photo-effects seen in a wide variety of semiconductors. Most of this work was unrelated to other work in the field because of poor reproducibility, results from similar experiments sometimes giving apparently contradictory results. However, the development of cuprous oxide rectifiers and photocells brought order to the field, and the subsequent development of a good theory of metal-semiconductor barrier effects was the climax of this early period.

During the second period, attention shifted to p-n semiconductor junctions. With the experimental results from these, theory could be verified to a degree not possible before, and the resulting understanding made possible the development of semiconductor devices and the practical realization of the present generation of solar conversion devices.

The order of presentation of the material in this history is chronological, but a division has been made into various subject fields, as shown in the index. This has been done to allow a coherent development of each topic. The potential difficulty with this method is that it does not show the interaction between contemporary developments in separate fields. These were, in fact, not strong during most of the early period, but where they did occur, cross-references will be found in the text.

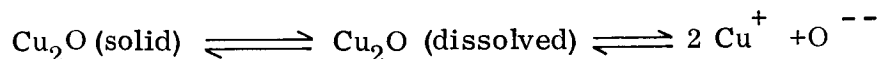
B. THE BECQUEREL EFFECT

Since the Becquerel effect is of some historic importance, but is judged to be unlikely to yield results of practical significance for power conversion devices, the account which follows does not aim to be an exhaustive study of the subject. Since most of the review papers are mentioned as such in the text, reference to these will provide a more extensive bibliography should this be desired.

The Becquerel effect is seen with two identical electrodes immersed in the same electrolyte solution, when one electrode is illuminated and the other is in darkness. A potential is developed between the electrodes, the voltage value increasing with light intensity. A current can be drawn from the cell, the short-circuit current value also increasing with increase of illumination. It is usual for the illuminated electrode to become electrically positive, but there are exceptions to this rule. In some systems (notably with cuprous oxide electrodes) it is necessary to "activate" the light-sensitive surface by passage of an electric current, before the photosensitivity is developed.

Becquerel's paper (1), published in 1839, marks the beginning of photovoltaic research. The paper is wholly concerned with experimental results, giving data obtained using platinum electrodes in solutions of hydrochloric acid, and brass and silver electrodes, also in acid solutions. It was found that silver halide coatings on the electrodes markedly increased the currents obtained, but that the action was a transient one. Simple spectral response measurements were performed using sunlight passed through a prism, the response peaking in the green for brass electrodes, and the ultra-violet for silver halide electrodes. Care was taken to distinguish the observed effects from any which might arise from thermal action, but no distinction was possible between purely photoelectric and photochemical reactions.

Following Becquerel, reports of further researches were made at various times during the remainder of the nineteenth century, the main contributions being a large increase in the number of electrode-electrolyte systems known to be photosensitive. Kochan (2) published a summary of the work up to 1905. Interest then shifted primarily onto Cu_2O -electrode systems, this being a precursor to the wave of interest in this material in the dry-rectifier photoelement work during the 1920's and early 1930's. Garrison (3) in 1923 reviewed the previous work in this field, and reported the results and conclusions of his own experiments. The principal difficulty lay in separating photochemical from physical photoelectric effects. Garrison's conclusion was that in the systems involving Cu_2O electrodes in neutral electrolytes (e.g., K_2SO_4 and KCl) the primary reaction is chemical, the light producing a displacement of the equilibrium in the reaction:



in such a way that Cu_2O was dissolved from the solid. Perhaps the most interesting point brought out in this paper concerns cell output potentials. It was believed that the Becquerel electrode action established a "concentration cell",¹ and, hence, a logarithmic dependence of cell output potential on illumination intensity is predicted, under reversible thermodynamic conditions, i.e., open-circuit conditions. Experimental verification of this relationship was sought and obtained with fair accuracy. This logarithmic dependence of V_{oc} on illumination intensity was apparently not known for barrier-layer cells until some ten years later.

¹ For an exposition on this subject, see any standard text on physical chemistry, e.g., Elements of Physical Chemistry by Samuel Glasstone, St. Martin's Press Inc., New York.

Winther's paper in 1927 (4) reviewed the work up to that date. From this review of the available data and theories it was concluded that incident light caused a primary ionization at the electrode-electrolyte interface (a pure surface effect) with a subsequent change in the adsorption equilibrium. Any photochemical process accompanying this physical process was considered to be a side effect. The lack of correlation between photoconductivity and photovoltage was thought to be due to one being a surface effect, the other a bulk effect, but an intrinsic connection was assumed.

In 1929, Winther (5) presented experimental work on Cu_2O electrodes in dilute KCl solutions. It was found that oxygen was consumed at these electrodes, and it was concluded that in these and other "oxygen-electrodes" a potential difference was maintained across the unilluminated Cu_2O , but on illumination, a drop in electrical resistance occurred which allowed a chemical reaction to take place, producing an emf relative to an unilluminated electrode. This apparent reversal of the author's view of his subject was caused by the great difficulty encountered in separating chemical and physical effects occurring simultaneously. This is probably the main reason why the work done on "dry" systems was to prove so much more effective in elucidating fundamental processes.

A considerable amount of research on photoelectric effects was conducted at Columbia University under C. G. Fink, during the 1930's. Some of the early work done during this period was on Cu_2O Becquerel cells, using $\text{Pb}(\text{NO}_3)_2$ electrolyte and Pb as a second electrode. (Such a device, of course, generates a dc voltage under no illumination.) Some of this work was published in 1930 (6), but the primary emphasis in this paper was on techniques for fabricating cells, and on discussions of their applications, so that the work is of minimal value to the development of this subject. Later work by Fink and Adler was to prove of greater significance.

In the years 1920-1932, the front-wall barrier Cu_2O cell was developed, and an understanding of its operation was obtained. A major part of this work was done at the laboratories of Siemens in Germany under Schottky, Duhme, Waibel, and others. It is clear that this group understood the relevance of their work to an explanation of the Becquerel effect, as is shown by a comment by Schottky (7), and in a review paper by Duhme (8) both published in 1931. This issue was taken up in detail by Waibel (9) in 1932. The experimental evidence produced by Waibel using Cu_2O electrodes in 5% KCl solution and Cu_2O barrier-layer photocells with a transparent conducting front electrode was as follows:

1. In both cells, photoeffects were seen only when the cuprous oxide surface was activated. This activation could occur by polarization in a liquid solution, or by passing a current through the cell from an external source. After activation, the same electrode showed photosensitivity in both types of cell.
2. The photocurrent in both cells was in the same direction.

3. The spectral sensitivity for both cells was the same.
4. The photogenerated currents were independent of the counterelectrode material in the barrier-layer cells, and the open-circuit voltages were dependent on the oxide resistivity in the same way for the two cells.

From this evidence, it was concluded that the Becquerel effect and the barrier layer photoeffect were fundamentally identical, although, of course, this was true only in the case of cells in which chemical reactions did not dominate the effects.

Independent work leading to the same conclusions was reported by Müller and Spector (10), the experimental evidence presented also being comparative measurements of the behavior of the two types of cell.

Further work was reported by Adler (11) in 1940. The interesting point brought out in this paper is the expressions which were derived for the dependence of the cell open-circuit voltage (V_{oc}) on illumination intensity (J). The analysis is related to that performed by Garrison in 1923, but with a starting point in reaction rate considerations. Again, the logarithmic dependence of V_{oc} on J is deduced for moderate and high light levels, but, in addition, the linear dependence of V_{oc} on J at low light levels is derived.

The general expression which was obtained for electrode potential V_e as a function of illumination intensity J was

$$k_3 J = k_2 [A] \frac{\exp -q\alpha V_e}{kT} \left[\exp \left(q \frac{V_e - V_o}{kT} \right) - 1 \right] \quad (1)$$

where k_2, k_3, α are constants,

$[A]$ is the chemical activity of atoms at the electrode surface,

q is the electronic charge, and

V_o is the dark emf of the cell.

It was shown that in the case where $(V_e - V_o) \gg \frac{kT}{q}$,

$$V_e = C + B \ln J \quad (2)$$

where B and C are constants.

When $q (V_e - V_o) \ll kT$, i.e., for low illumination intensities, or for metal electrodes which produce only low voltages under high illumination intensities:

$$V_e = C' + B' J \quad (3)$$

B' and C' are again constants.

The same analysis was presented in another paper by Fink and Adler (12), and further discussion of the points raised is given in a letter published in 1941 (13) in reply to criticism, no new material being presented.

This is as far as we shall pursue this subject at this time. Two main points are to be made concerning the work which has been reviewed.

- (1) The Becquerel effect was the earliest photoelectric phenomenon to be studied.
- (2) The theoretical interpretations offered by the physical chemists were much in advance of work done by those studying purely physical effects. If these results had been combined with the electrical equivalent-circuit work done at the same time, a quantitative understanding of the barrier-layer cells could have been arrived at much sooner than was actually the case.

C. BARRIER PHOTOVOLTAIC EFFECT

1. Discovery and Experimental Work

The earliest work on photovoltaic effects at potential barriers was done with selenium devices, and was reported in 1876, by Adams and Day (14). Both photoconductive and photovoltaic effects in selenium were investigated and used for many years, selenium being the most photosensitive material known until the advent of p-n junction devices in the 1940's. However, the better reproducibility and stability of devices based on Cu_2O , coupled with improved electronic techniques which compensated for their lower sensitivity, partially moved attention away from selenium after about 1930. The work on copper oxide barrier-layer cells proved to be the most important contribution both to the application of photovoltaic effects and to an understanding of the mechanisms of the effects. During this phase of the photovoltaic work, almost all of the concepts used in the manufacture and performance analysis of present-day solar cells were developed.

a. Selenium: Adams and Day (14) studies both photoconductive and photovoltaic effects in bulk selenium specimens in the form of small rods, with platinum contacts sealed onto the ends of the rods by heat. The specimens were annealed before use causing partial crystallization of the selenium, to give low electrical resistivity. The results showed that:

- (1) The apparent resistance of the specimen diminished as the applied voltage increased.

- (2) The potential first applied to a specimen could cause an asymmetry in the electrical conduction for all later measurements, the direction of initial current having the higher resistance.
- (3) Passage of a current increased the electrical resistance of the specimen to further currents in the same direction, and reduced the reverse resistance.
- (4) On cutting off an externally applied current through a specimen, a small current in the opposite direction could be generated by the specimen.

These observations are apparently all explicable in terms of barrier effects at the contacts, together with trapping in the bulk.

On examining the effect of light on the specimen, a general increase in conductivity was observed, except in some cases where a drop or even reversal in specimen current was obtained. This suggested that the light was generating a potential in the specimen, a supposition which experiments proved to be correct, the illumination from a single candle being enough to produce an observable current.

Further experiments, using light filtered through water to remove infrared and in finely focussed beams, established the following points:

- (1) The effect was not thermal.
- (2) The sensitivity was different at different parts of the specimen.
- (3) When the platinum contacts were illuminated, current passed from the selenium to the platinum.

The interpretation offered was not that accepted today, but involved photo-activated crystallization of the selenium. Thus, it is seen that these authors observed all of the fundamental phenomena which made selenium such an interesting material for both research and technological purposes in later years.

Commercial application of selenium photoconductor cells to photometry soon followed, and methods for making more sensitive devices were devised. This work greatly improved fabrication methods; all of these points are well exemplified in publications by Fritts in 1883 (15) (16). It seems likely that Fritts saw photovoltaic effects in his work, but because of his concentration on making a practical photoconducting device, his work is of little significance for later photovoltaic developments. It does not even seem to be possible to deduce from his papers the construction methods adopted for his devices.

However, a paper by Uljanin (17) in 1888 gave details of a construction method which was remarkably effective. Here, semi-transparent electrodes of thin metal films were deposited on two sheets of glass, and the selenium was melted and squeezed out into a thin layer between the glass sheets. The cell was illuminated through one of the glass surfaces, and current was drawn from the cell by the two thin-film electrodes. The arrangement, of course, gave a very sensitive device.

A most interesting paper was published in 1917 by Kennard and Dieterich (18). Results were presented from a series of experiments in which surface potential changes were measured. The specimens were both selenium and cuprous oxide. We shall return to discussion of this paper in greater detail in the section on cuprous oxide photovoltaic effects; in the present context, it is sufficient to note that the surface potential was found to increase rapidly with increase of illumination intensity at low light levels, and progressively less rapidly at higher light levels. A later report by Kennard (19) presents experimental results on the changes in surface potential of selenium specimens under illumination by light of various wavelengths. The response was found to be insensitive to wavelength, and the potential change was found to vary approximately as the cube root of the illumination intensity.

The importance of selenium photovoltaic devices of the period is put into perspective by a publication by Lange in 1931 (20), in which comparisons are made among PbS, Cu_2O back-wall, Cu_2O front-wall and selenium cells. The sensitivity of the selenium cells ($0.3 \text{ mV lux}^{-1} \cdot \text{cm}^2$) is shown to be more than an order of magnitude higher than that for even the best Cu_2O cells.

The temperature sensitivity of the photocurrent output for the selenium cells was an order of magnitude less than that for the Cu_2O cells, in the region around room temperature. In spite of the technological importance of the selenium cells, the physics governing their operation was little understood. This is also made clear in Lange's paper, where a photoemission theory is advanced. Basically the same material was presented by Lange in several papers published in 1930 and 1931 (21, 22, 23), the development of front-wall cells of Cu_2O being of great interest during this period. It seems that those working on these Cu_2O front-wall cells realized that the basic idea (of applying a semi-transparent metal film electrode to the illuminated surface of the cell, using the sputtering technique) was applicable to other semi-conductors, presumably because of the similarity of the structure to that developed by Uljanin, but the first paper presenting results on such a selenium cell was by Bergmann in 1931 (24). The cell construction described consisted of a thin layer of selenium on an iron substrate, with a semitransparent metal film applied to the exposed selenium surface. Lead, gold, and silver films were tried as electrode materials, gold and silver giving the best results. The spectral response of such a cell is shown in Bergmann's paper, with a peak at 6150 \AA . The measured sensitivity was shown to be greater than that of front-wall Cu_2O cells by a factor of 3.5, with even greater sensitivity at low temperatures.

Bergmann also published the results of a series of experiments aimed at testing those theories of the optics of metals which analyze the effect of angle of incidence and angle of polarization on the absorption and reflection of light from metal surfaces. This paper (25) shows the experimental results to agree with those of the theory:

- (1) Polarization parallel to the metal surface gives a higher photocurrent than perpendicular polarization (except at 0° and 90° angle of incidence).
- (2) The photocurrent for parallel polarization peaks around an angle of incidence of 75° .
- (3) The photocurrent for perpendicular polarization falls off monotonically with increasing angle of incidence.

Small departures from the theory were ascribed to cell surfaces not being ideally planar.

A great deal of work on selenium cells into which small amounts (up to 10%) of sulfur were incorporated was done at the National Physical Laboratory, England, by Barnard during the 1930's (26, 27). The sulfur facilitated the preparation of the cells, without apparently altering the performance to any great degree. Various metals were used as sputtered film counterelectrodes, but the high work-function metals such as platinum, silver, and gold were found to give best results, platinum particularly yielding high open-circuit voltage values. In spite of the fact that the primary function of the research was to provide selenium cells for application to lighting-method studies in buildings, it was appreciated that obtaining adequate understanding of the cells' operation, by correlating theory and experiment, would ultimately yield improvements in photometry techniques. Consequently, the major discussion of these papers is to be found in the report section devoted to development of photovoltaic theories.

During the period covered, there were other papers on selenium cells, but these were primarily devoted to theoretical aspects of the subject, and so they also are to be found in the theory sections of this report.

This account of the history of selenium photocells has presented an account of the development of the manufacture of the cells. Their importance as photovoltaic cells is now largely historical, but their very high sensitivity made their use widespread for photometric applications, and they served their purposes well even when their properties were only known empirically. There appears to be an interesting analogy with the present use of selenium in the xerographic process, which is still not fully understood.

b. *Copper Oxide*: Although Grondahl is usually ascribed the honor of having discovered the photovoltaic effect in cuprous oxide, it is interesting to note that the effect was seen by Kennard and Dieterich (18) in 1917, ten years before Grondahl's discovery. Kennard and Dieterich's paper gives results from experiments in which surface potential changes under illumination were measured by means of the condenser method², or by an "ion contact capsule"³ method. The experimental arrangement used for measurements on cuprous oxide is illustrated in Figure 1. It is a little difficult to understand how the readings were taken, but it appears that two distinct groups of measurements were obtained. In one case, a potential of 20 mV was measured between contacts 1 and 2 even in the dark, and this potential was increased by some 7 mV when the whole top surface was illuminated, but decreased by the same amount if the contact area was shaded. In the other case, contacts 1 or 2, and 3, were connected to the measuring instruments (a potentiometer, with a quadrant electrometer as a null detector), and a surface potential change of +20 to +28 mV under illumination was measured. The first group of measurements indicates that photovoltages were being observed in an experimental arrangement essentially the same as that developed later by Grondahl, but it is also clear that the reported facts leave several questions unanswered, and the authors of the paper also indicate that they could offer no likely suggestion for explaining the observations. Probably because of these uncertainties, the work appears to have aroused little or no interest among those making photosensitive devices.

Hence, Grondahl and Geiger's paper (28), published in 1927, is generally taken as the first report in which photovoltaic effects in copper-cuprous oxide junctions are mentioned. (In the years immediately following, there appears to have been some confusion as to who first reported the effect, some authors having ascribed the discovery to Lange. However, Grondahl's letter (29) drew attention to his mention of the effect before Lange's publications.)

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- ² The method was first described by Lord Kelvin, and can be summarized as follows: The specimen forms one plate of a parallel-plate capacitor, the other plate being a flat metal electrode which can be vibrated at a known frequency and constant amplitude in a direction normal to the specimen surface. The capacitance of the arrangement thus oscillates at the driving frequency of the plate, so that a constant electric charge existing in the capacitor causes an alternating voltage to appear across the capacitor terminals. The charge in the capacitor is determined by the surface potentials of the two plates of which it is composed. Hence, if illumination causes a change in the surface potential of one of the electrodes, a change in amplitude of the ac signal is produced by the apparatus. Absolute surface potentials cannot be measured by the method, which is applicable only to changes in surface potential. The equipment and its use are subject to many precautions; see, for example, Many et al. Semiconductor Surfaces, John Wiley and Sons, Inc., New York.
- ³ Contact to the surface of the specimen was produced by mounting a copper strip coated on one side with polonium in an insulating ring such that when the ring was placed on a flat surface, the uncoated side of the copper was adjacent to the specimen but not touching it, and the polonium-coated side was uppermost. The top of the insulator ring was covered with a metal gauze which was connected to the measuring instruments, and a mica window was sealed over the top of the gauze.

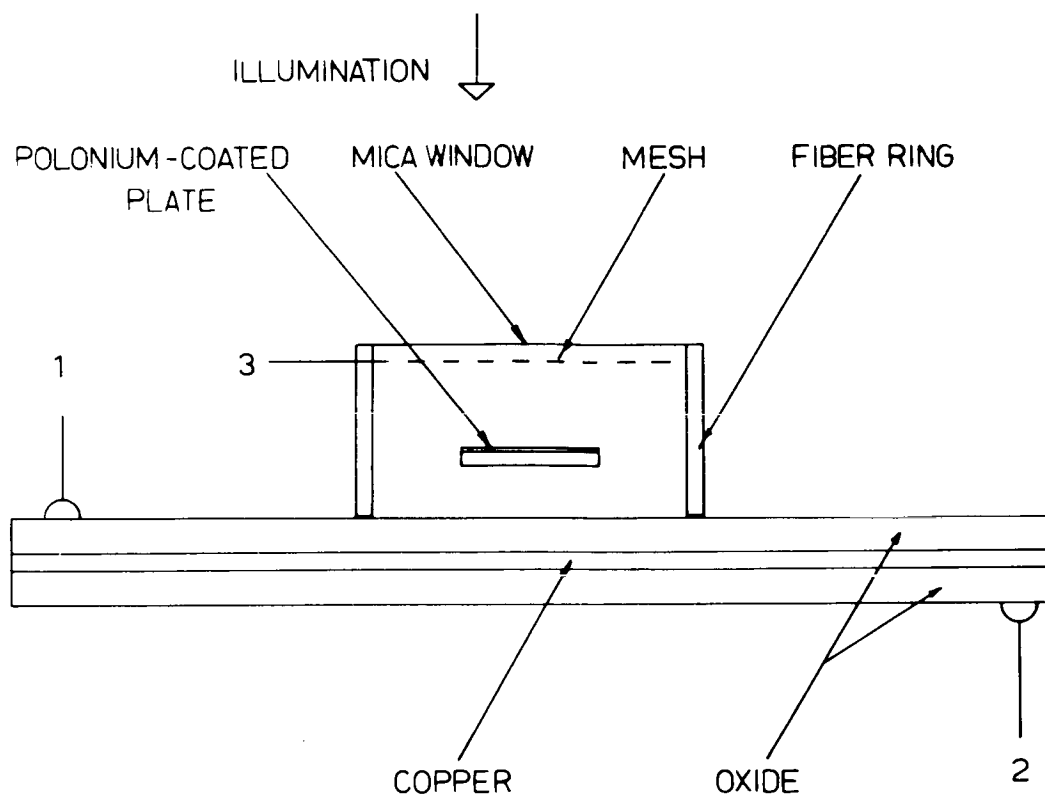


Figure 1. Experimental equipment of Kennard and Dieterich.

Grondahl and Geiger's 1927 article was devoted to an account of the characteristics and applications of the copper-cuprous oxide rectifiers invented by Grondahl in the previous year. The rectifiers were made by oxidizing one surface of a copper disk to produce a cuprous oxide layer 1.5 to 2.0 mils thick. A counterelectrode was applied to this oxide layer by pressing a lead disk tightly against it. The story is recounted by Wilson (30), that the performance of a rectifier assembly was found to alter during outdoor operation, when a shadow fell on the rectifiers. Investigation of this effect was the basis for the remark made by Grondahl and Geiger (p. 363) "For use with very sensitive instruments, the rectifier should be protected against illumination. Illumination not only changes the resistance, but produces a small emf in the rectifier." The method of construction employed in these rectifiers limits the photosensitive area to the edge of the cuprous oxide layer. Hence, it seems remarkable that the sensitivity for this type of cell, quoted by Grondahl in 1933 (31) as 15 to 20 mA for 2000 lux (equivalent to about 5.1 to 6.8 mA under sunlight illumination), should have been observed.

A much more suitable form of construction for photosensitive devices was soon developed, the same general form being arrived at by several workers independently. The earliest change was to replace the opaque lead contact disk with a special lead wire pressed against the oxide with a glass plate. Thus, the cell could now be illuminated normal to the plane of the oxide rather than around the edge only, and a larger sensitive area was obtained. However, this construction gave a rather high series resistance.

Consequently, there were quickly developed alternative methods of applying a collector grid to the cells. These methods all resulted in a metal film grid being produced on the oxide surface. This was done either by sputtering a metal such as copper or gold onto the surface or by chemically reducing a portion of the oxide film at the exposed surface. The desired grid pattern was then produced by etching out regions of this film. The sputtered films gave the better results, so that this method came to predominate.

The photosensitive region of these cells was shown to be localized near the copper-cuprous oxide interface by Schottky (32) in 1930. (It appears that work on Cu_2O photocells had been progressing at Siemens in Germany independently of the work at Westinghouse in the U.S. under Grondahl. Presumably, both companies realized the commercial possibilities of the devices, and for this reason delayed publication of scientific papers until patent rights had been established. Thus, a patent application on the use of Cu_2O grown on a copper base in a photocell was filed by Westinghouse in 1926, before the first reference to the effect in the literature, by Grondahl in 1927.)

To demonstrate that the photocurrent was not being generated at the counter-electrode to oxide interface, Schottky performed an experiment in which a fine light beam was moved away from the edge of a gold electrode sputtered onto the surface of an oxide layer burned on a copper plate. An exponential drop of current with increasing distance was found, with a decay length of 3.8 mm. This correlated with calculations of a decay length of 4.2 mm using the equivalent circuit described in the later section of this report which deals with theory. The experimental results hence confirmed that the current generation was localized in the barrier layer region. This work by Schottky, and the relevance of his analysis to present-day work on photodiodes, has been discussed recently by Emmons (33).

The last section of Schottky's paper describes a most important innovation. Apparently as a result of the experiments described in the previous part of the paper, it was discovered that a barrier-contact could be made to the oxide layer by a semitransparent sputtered metal film; see Figure 2. Schottky distinguished the two different types of cell by the terms "Hinterwandzelle" (back-wall cell) and "Vorderwandzelle" (front-wall cell); this terminology came into general use, sometimes appearing in the abbreviated form of "H-cell" and "V-cell". As is pointed out by Schottky, the thin-film counterelectrode is not advantageous electrically, since it produces a high electrical resistance, but it is very effective optically, since the photoelectron density is higher near the front surface of the Cu_2O than near the back surface. The high electrical resistivity was overcome by the use of grids, to provide a structure closely resembling the barrier-layer solar cells under investigation today.

Another publication on front-wall cells was made by Duhme and Schottky (34). The cells reported were made by deposition of gold and silver counterelectrodes on etched

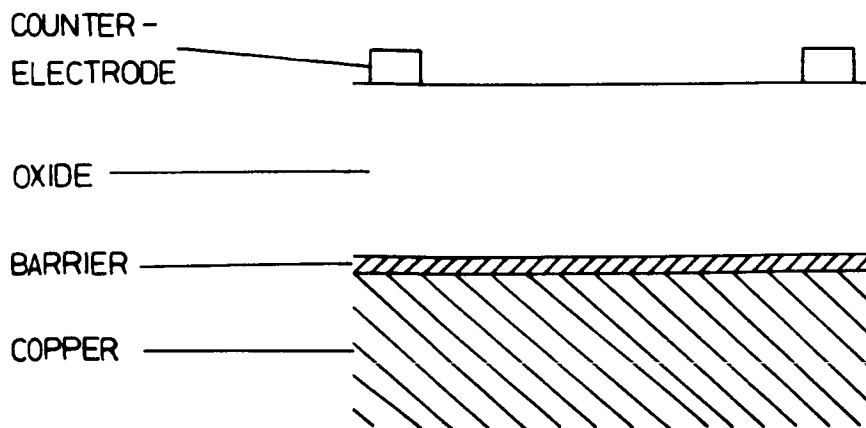


Figure 2(a). Cross section of Cu_2O back-wall cell.

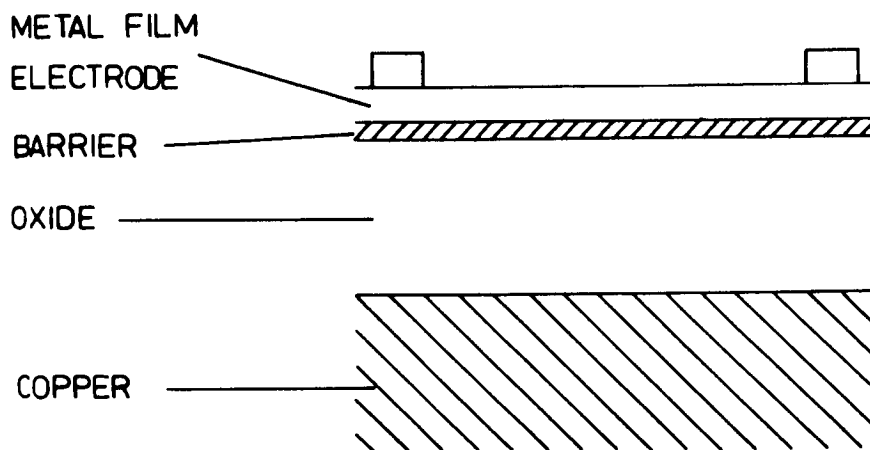


Figure 2(b). Cross section of Cu_2O front-wall cell.

Cu_2O plates. These cells were ten times more sensitive and had a reverse resistance 1000 times higher than previous back-wall cells. Calculation from the reported data indicates that these cells would have a short-circuit current density of about 34 mA cm^{-2} under 100-mW cm^{-2} sunlight. The quoted series resistance figure of 700 ohms-cm^{-2} almost certainly includes the effective resistance of the diode, since the analyses of the day did not provide a diode characteristic, and since it was usual to regard the diode as a photoconductive resistor.

Perhaps the most important contribution of Schottky, however, was in elucidating the mechanism of operation of the cells. Both Schottky and Grondahl independently made measurements on the voltage drop occurring across the oxide layer (in the direction of current flow) during operation of a copper-cuprous oxide rectifier.

These measurements required careful manipulation of a very fine probe across the exposed edge of the oxide layer, but both workers came to the same conclusion, that the major part of the voltage drop occurred in a very narrow region at the oxide-bulk copper interface. This region was so narrow that the probes could not resolve its thickness. Since it had been established that bulk cuprous oxide exhibits only ohmic conduction, this identification of the barrier layer resolved a major unknown in the operation of the cells. This barrier layer was first identified by Schottky, who applied the term "Sperrschicht", which was later used by some English-language authors to identify photocells of the barrier type.

Schottky also correlated his probe measurements with capacitance measurements by Deutschmann on Cu-Cu₂O junctions (35); the capacitance was found to vary with applied bias voltage, but a satisfactory analysis of this effect was not made at the time.

On the technical level, Schottky also found that it was necessary to activate the Cu₂O surface before deposition of the counter-electrode to provide photosensitivity in the front-wall cells. It was probably fortuitous that a glow discharge was found to perform this activation, since this process would also take place during the sputtering operation.

A large amount of work was also done at this time by Lange. This was largely directed toward applications, a major effort being made to provide useful photometric instruments. Lange appears to have been very unfortunate in not being the first to make any of the major discoveries in this field, since it appears that he independently observed many of the effects before reading of the work of others (particularly Grondahl). His subsequent publications mainly review the subject (23, 36) so far as they deal with the photovoltaic effect. On applications, however, several interesting suggestions are made. Quoting verbatim from a translation of reference (23): "Based on our knowledge of the effect, a direct conversion of light into useful electrical energy is possible. However, all the experiments conducted up to now have resulted in little progress toward realization of such a conversion. Using a more appropriate semiconductor for the intermediate layer, it will be possible to select the cell effectiveness for a specific spectral region. Use of a more appropriate unipolar layer is expected to give a further increase in the efficiency of the cell. It is then possible that efficiencies can be reached which allow direct conversion of light into electrical energy."

His remarks concerning matching of the semiconductor to the spectral distribution of the source are highly pertinent to present-day solar cell research, even though the remarks were based on a theory of cell operation now known to be incorrect.

Simple experiments on electrical characteristics of Cu₂O rectifier cells were reported by Graffunder (37). The results eliminated the possibility of the effects seen being

thermoelectric. For Graffunder, the main surprise was the direction of current generation. The consistency of the direction was carefully checked experimentally, both for Siemens rectifiers and for American-manufactured devices (presumably Westinghouse units). The generated current was always found to be in the high-resistance direction through the rectifier, a point which had been explained by Schottky, and which will be taken up later in this report. An experimental I-V curve for a rectifier is shown in the publication; the curve shape is good. The effect of bias voltage on the external current of the device under illumination was also investigated, but the results apparently did not show this I-V curve to be correlated with the unilluminated curve, probably because of series resistance and photoconductive effects.

A major contribution to experimental knowledge of back-wall Cu_2O cells was made by von Auwers and Kerschbaum (38). These workers were mainly concerned with arriving at an electrical equivalent circuit for the cells, and at elucidating the physical mechanisms underlying their operation. Their theoretical analysis will be dealt with elsewhere; experimental results were presented graphically showing the relationships between cell voltage, current, apparent resistance, illumination intensity, distance of illuminated region from counter-electrode edge, thickness of oxide layer, and proportion of cell illuminated. Many graphs were plotted on both linear and logarithmic scales, and some of the relationships were measured using filtered illumination to provide light of different wavelengths. It was established conclusively that the short-circuit current was linearly related to light intensity, but this is really the only significant numerical result given. It seems that once again internal resistance and perhaps photoconductivity in the oxide prevented the exponential variation of V_{OC} with illumination intensity from being discovered.

Another conclusion drawn from the experiments was that the open-circuit voltage was not linearly related to illumination intensity. Perucca and Deaglio (39) reported experiments indicating that both V_{OC} and I_{SC} were related linearly to illumination intensity. The other results in their paper show that the specimen resistance was very high, thus leading to an almost linear I-V characteristic. This same point was also noted by von Auwers and Kerschbaum in a reply to Perucca and Deaglio (40); working from present-day concepts of the cell equivalent circuit, the reason for the discrepancy in observations is clear.

Kerschbaum published some results obtained during an attempt to separate the photovoltaic effects from photoconductivity in the specimen (41). The method relied on the two effects having different time constants, the specimen being illuminated by a chopped light beam. A graph is given showing photovoltage as a function of illumination chopper frequency at various values of applied bias voltage. The results were inconclusive, and this measurement approach was apparently not investigated further.

The first of a series of measurements of the dependence of photoelectric properties on temperature between 300° and 170°K were made by Teichmann in 1930 (42), and the temperature range of these measurements was extended to 120°K as described in later publications (43,44). The specimens used were back-wall cells made from commercially available rectifier plates. The cell resistance and open-circuit voltage were found to increase between about 200° and 170°K. The short-circuit current was also found to increase to a maximum between about 190° and 130°K, but then showed a very sharp drop and a small reverse current at lower temperatures. It seems probable that some of the effects seen were thermoelectric in nature, since the construction of the equipment appears to be such that appreciable temperature gradients could be present in the cell.

Lange, noting Teichmann's work, repeated the measurements on temperature effects, and reported results obtained with both front- and back-wall Cu_2O cells, and selenium barrier-layer cells (21). For the back-wall cell, the same general behavior of the photocurrent as seen by Teichmann was observed. However, the photocurrent was found to peak at a rather higher temperature (about 200°K), and the decrease at lower temperatures was not as sharp and did not reverse. Lange explained the latter difference as arising from the construction of Teichmann's specimens, which would permit some front-wall effect to occur. The photovoltage was found to increase almost exponentially with drop in temperature down to about 150°K.

The cell resistance was also found to increase rapidly with lowering of cell temperature. Lange expected an exponential dependence of free electron concentration on temperature because of a model which would not generally be accepted today, but which assumed Maxwell-Boltzmann statistics. As a consequence, the logarithmic dependence of cell resistance on reciprocal temperature which was obtained experimentally agreed with the theory. However, the results showed two linear regions of dependence, with a breakpoint at about 200°K; this behavior was ascribed to a phase transition in the cuprous oxide, rather than a change of activation energy. (In these back-wall cells, the bulk resistance of the cuprous oxide was high and tended to dominate the effective resistance of the diode.)

For the front-wall cells, the same rapid increase in photo-emf with decreasing temperature was observed. However, the short-circuit current decreased monotonically with drop in temperature, rather than exhibiting a peak, and Lange ascribes the difference between the cells' behavior to the lower bulk resistance of the Cu_2O in the front-wall cells.

This paper by Lange also contains results of spectral response measurements on front- and back-wall cells. Further results were published by the same author (22). For the back-wall cells the response was found to depend on the oxide film thickness

which acted as a red filter, giving a peak at 0.63 micron and a cut-off at 1.4 micron. Front-wall cells were found to peak at a shorter wavelength, 0.54 micron, and to be more efficient. This spectral response for the front-wall cells was found to coincide with that for the photoconductive response, with a peak in the region of the highest optical absorption.

For Lange, the main importance of the results was their significance in photometric work, and PbS and Se cells are included as well as Cu_2O cells. Similar results were presented in the same year by other groups, for whom the main interest lay in elucidating the scientific aspects of the cells.

Schottky (45) presents results attributed to Waibel, who measured the spectral response of Cu_2O cells. These results were particularly valuable because they showed absolute quantum yield, i.e., number of electrons crossing the barrier per photon absorbed in the Cu_2O (allowance was made for loss of photons in passing through the metal film counterelectrode). These data were correlated with optical absorption measurements made on Cu_2O , and Schottky deduced from these that the diffusion length for photo-produced electrons could be much larger than the mean free path. He remarks that he felt that the barrier photovoltaic effect may be largely governed by the diffusion process. Auger and Lopicque (46) reported spectral response measurements on Cu_2O front-wall cells, showing results obtained with both silver and gold counterelectrode films produced by sputtering. They also measured the optical transmission of films of these metals sputtered onto glass, and, hence, could calculate the spectral response of the cells relative to the amount of light entering the oxide. The results showed the response to be independent of counterelectrode material.

Dubar (47) took up a point suggested by Auger and Lopicque, and measured the response of a back-wall cell, showing that the response occurred only for illumination wavelengths longer than the absorption edge of the oxide layer. The response peaked very close to the absorption edge around 6000 Å but showed a considerable response even at 12,000 Å.

In 1931, Duhme (48) considered the experimental results obtained with Cu_2O front-wall, back-wall, and Becquerel cells, and showed that all the cells worked in fundamentally the same way; i.e., all exhibited the barrier-layer photoeffect. Also in 1931, Lange (20) reviewed the history of the development of Cu_2O cells, and proposed various photometric arrangements for which the new cells would be suited.

In 1932, Waibel and Schottky published two related papers (49, 50), which report results correlating rectification ratios and photovoltaic output. The ion bombardment method of activation of the Cu_2O surface prior to deposition of the barrier-layer electrode, combined with a chemical etching technique, enabled these workers to make cells with characteristics varying from ohmic conduction to rectification ratios of 20:1 at 2 volts bias. These specimens showed that the more highly rectifying

cells gave much higher photosensitivity. One interesting fact was reported in the latter reference: Some highly rectifying cells, under high bias conditions, showed quantum efficiencies 100 to 1000 times larger than in the usual photovoltaic operation. These quantum efficiencies must have been much higher than unity, and are presumably due to photoconductive gain.

The difference in conductivity between cuprous oxide prepared for rectifiers and that as used in front-wall photocells has already been noted. The reasons for this difference were investigated by Dubar (51). Chemical analysis, transmission microscopy, x-ray powder diffraction, examination of electrolytically deposited films on the oxide surface, and electrical resistance measurements on individual crystallites and on compressed powders were all used. From these measurements it was concluded that the two different types of oxide have the same chemical composition and the same crystal structure within the measurement accuracy. It was also observed that the electrolytic deposits followed the crystallite grain boundaries preferentially, indicating that these are electrically conducting regions.

Rupp also investigated the conduction process in the copper oxide of operating photocells (52). The short-circuit currents in the cells under steady illumination were measured as a function of the direction and intensity of an applied magnetic field. Variations were found across the surface of an individual cell, and from one cell to another, but the results showed that the decrease in current and increase in the cell's apparent resistance were generally maximum for a field direction parallel to the plane of the cell, and minimum for a field direction perpendicular to the cell plane. A change in the free path of electrons under the magnetic field influence is noted as an explanation of the effect.

Very similar work to that being done elsewhere was also in progress at the Soviet Union's Central Research Laboratories. Results were presented in the first issue of Physikalische Zeitschrift der Sowjet Union, in 1932, partly as abstracts of conference papers (53, 54) and partly as full papers (55, 56).

Lepeschinskaja (53) described methods used for the manufacture of cells, and there is no indication that these differed in any way from those made elsewhere. Measurements were made on the I-V characteristics, and the dependence of I_{SC} and V_{OC} on illumination intensity. Once again a linear dependence of I_{SC} on illumination intensity was found.

A rather more ambitious series of experiments was reported by Kurtschatow et al. (55, 56). Systematic spectral response measurements of both photocurrent and photovoltage in Cu_2O cells were performed. The influence of the metals (Ni, Cu) used for the top electrode was studied as were the contributions of the front-wall and back-wall effects, and the effect of temperature. A spectral response peak at 0.55 micron is associated with the front-wall effect, and a peak at about 1.0 micron with the

back-wall effect. Correlation between photovoltaic and photoconductive response was seen. (The results are closely parallel to the other spectral response measurements described above.) The second paper deals mainly with advancing and testing a hypothesis of cell operation, and will be dealt with in the theory section of this report.

Sinelnikow and Walther (54) described an apparatus for the automatic recording of the spectral distribution of photocell sensitivity, using a monochromator synchronized with a recording galvanometer. Methods for the automatic recording of I-V characteristics were also described.

An extensive historical account and review of Cu_2O rectifiers and photocells was given by Grondahl in 1933 (57), together with an extensive bibliography. Essentially no new experimental results are presented. Indeed, the period of experimental work was now mainly over, the characteristics of the effect having largely been determined.

The published literature which has been reviewed does not give a clear description of the fabrication methods used for the cuprous oxide devices, probably because of commercial competition. However, some of the more academic workers such as Fink (58) discuss fabrication methods, and there is no reason to think that the industry used noticeably different techniques. The copper plates were surface cleaned, and then heated in an electric furnace to a little over 1000°C , to form the oxide layer. The period of heating and the furnace temperature were critical, since cupric oxide is formed below 1040°C , and copper melts at 1083°C . Between these temperatures, cuprous oxide is formed as a glassy layer on the metal. After four minutes in the furnace, the copper plate was lowered quickly into a water bath. Sheets of 6 in. x 10 in. were processed in this way by Fink; Schottky mentions the use of plates 40 cm x 60 cm (~ 16 in. x 24 in.) in Reference (32), but this is probably a misprint, since in Reference (59) the specimen size is given as 40 mm x 60 mm.

Although such large sheets could be produced, the application of cuprous oxide to present-day solar energy conversion does not appear feasible, because of the low efficiencies which can be obtained with this material, as was shown by theoretical analyses during the 1950s. An essential part of the structure of the cuprous oxide rectifier and photocell is the presence of a region of high-resistivity oxide at the metal-oxide barrier. This material is stoichiometric cuprous oxide, whereas the bulk of the oxide layer contains a very small excess of oxygen, which increases the carrier concentration, and hence the conductivity, by several orders of magnitude. The effect of this particular structure is to produce a "Mott barrier," as discussed in the theory section of this report.

Fink and Fogle published a very lengthy paper in 1934 (58), presenting no fundamentally new data. However, the paper appears to be historic in one respect: It contains the first mention of the use of an antireflection coating. The effect was discovered

by accident, when it was found that application of beeswax to a cell, for masking during chemical etching, increased the cell output current. The possibilities of the effect were fully explored, with analyses of the effect of various coatings on various types of cell. (These coatings were not of the modern quarter-wavelength interference type.)

This concludes the history of the experimental work on cuprous oxide cells. Quite aside from the technological importance of the cells, the cells are important historically because it was largely on the experimental data from these cells and the rectifiers from which they were developed that the modern theory of semiconductors was first based. This mainly seems to have been because the effects seen with cuprous oxide could be more readily reproduced than with any of the large number of other materials in which photoelectric effects were seen. It was presumably because of the strong applications-oriented groups working in Germany under Lange and Schottky, and in the U.S. under Grondahl, that empirical knowledge of the effects ran considerably ahead of the theory for some years. It is for this reason that the experimental work has been presented first in this historical review.

c. *Other Materials:* From the time of the earliest work on selenium during the latter part of the 19th century, photoelectric effects were seen in a wide variety of semiconducting materials. However, because of a general lack of reproducibility, these observations did not contribute appreciably to the knowledge of photovoltaic effects which was being built up by the study of selenium, and later of Cu_2O . Since the materials under consideration were compounds, and the specimens were often naturally occurring minerals, the reasons for a lack of reproducibility are not hard to understand. Some of the materials which were studied have received further attention rather recently in pick-up tube research and IR detector development, and even today it is very difficult to obtain reproducible results with these compounds.

Of the various materials studied, Ag_2S gave the most consistent results. Photovoltages at metal contacts to crystals of the naturally occurring mineral argentite (Ag_2S) were measured by Geiger et al. (60, 61) in the early 1920's. The contacts were pressed knife-edges, and the results were found to be independent of the metal used. The generated emf reversed on moving the illumination to the other contact. Experiments showed an increase in photo-emf with intensity of illumination, which was linear at low intensities and reached a saturation value of 0.013 V at higher intensities. Using a monochromator with a thermopile for power measurements, the spectral dependence of the emf was measured and found to peak sharply around 1.0 micron.

The emf was also found to "fatigue" after extended illumination periods, falling to very low output values and sometimes even reversing. This effect may arise partly from trapping, or may be due to field-assisted diffusion of electrically active impurities. Effects such as this are frequently seen during present-day work on the less-well-known compound semiconductors used for sensing devices.

Geiger also found photovoltages to be exhibited by proustite (Ag_3AsS_3), molybdenite (MoS_2), stephanite (Ag_5SbS_4), and acanthite (Ag_2S); all with knife-edge contacts. This list gives some idea of the type and range of compounds which were investigated during this period. Significantly, Geiger also found that some (but not all) cuprite crystals (Cu_2O) exhibited photovoltages, under the same experimental conditions. The difference between this observation, with its uncertainties and nonreproducibility, and the work done later by Geiger and Grondahl, well exemplifies the great advantage which was inherent in the specimen preparation techniques devised by the Cu-Cu₂O rectifier work.

After the development of the work on Cu₂O cells, Lange (20, 23) realized that effects which he had seen at metal point-contacts to PbS crystals were of the same nature as those seen in the barrier-layer cells.

Research on a remarkably large number of minerals and compounds was reported in 1936 by Bergmann et al. (62). The measurements of spectral sensitivity were performed using methods developed by Bergmann (63), in which a chopped light beam was used to generate an ac photovoltage, which was taken from semitransparent metal film electrodes on the crystal to the input of an electronic amplification and measurement system. A full tabulation of the 37 compounds in which photovoltages were measured is unnecessary in this context, but some are worthy of special mention. The spectral response of CdS is shown, with a peak at about 4800 Å and a long tail into the red, rather similar to the response measured in CdS solar cells today. The spectral responses of a series of alloys of varying composition in the BiI₃: PbI₂ system show a graded response through the range 4500 to 6500 Å, the relative responses at the ends of the curve being proportional to the composition of the alloy. This result is the direct precursor to present-day work aimed at producing materials with forbidden-band values which can be adjusted by changing an alloy composition. However, it seems that for some of Bergmann's results, there is the possibility that the specimens were not of the compositions noted, but were of varying stoichiometry and not of a single phase. Another interesting point in this work is Bergmann's mention of photovoltaic activity in organic dyestuffs. Unfortunately, the response obtained was very small, so that spectral measurements could not be made. However, this appears to be the earliest mention of semiconducting effects in organic materials.

This account covers the major points which were established experimentally before 1940. Because these compounds have contributed little to the development of the subject, no attempt has been made to treat the matter exhaustively.

d. Summary of Experimental Results: Before going on to an account of the development of the theory of the photovoltaic effect, it will perhaps be helpful if a summary is given of the major points established experimentally prior to 1934.

- (1) Potential differences of up to a few tenths of one volt can be obtained by illumination of a metal-to-subconductor⁴ boundary.

⁴Semiconductors were recognized during early work by their negative temperature coefficient of resistivity.

- (2) The effects seen, and particularly the magnitude of the photo-emf, were sensitive functions of the methods used to prepare the specimen.
- (3) The effects were usually associated with a nonlinear, and sometimes with a rectifying, type of I-V characteristic.
- (4) The short-circuit current was proportional to the light intensity.
- (5) At low light intensities, the open-circuit voltage was proportional to light intensity.
- (6) At medium light intensities the open-circuit voltage was known to be a logarithmic function of illumination in Becquerel cells, but an unknown and nonlinear function of light intensity in solid barrier layer cells.
- (7) At high light intensities, the open-circuit voltage approached a saturation value.
- (8) The normalized spectral response of any given cell type was much more consistent than the absolute response of the cell, and was characteristic of the semiconductor of which the cell was made.
- (9) The potential drop in the rectifying effect occurred in a region of sub-microscopic thickness at the metal-to-semiconductor boundary.

2. Barrier-layer Photoeffect: Development of the Theory

a. Introduction: It is useful to divide the theory of operation of photocells into two parts, one part dealing with the fundamental physical processes involved, and the other dealing with the electrical network analysis theory which provides the electrical equivalent circuit for the cell. Most of the work done on photocells before about 1920 was by physicists and so it is natural that theoretical work from this period should be mainly concerned with physical fundamentals. However, without the electrical circuit analysis, theorizing was extremely difficult, and the results from this very early period bear little relationship to our present concepts of cell operation.

The subsequent work on Cu_2O cells was performed mainly by electrical engineers (Grondahl, Schottky, and Lange, among others), and one of the major achievements during this phase was the development of valid equivalent circuits for the cells.

In fact, our present ideas in this area are based almost entirely on circuits developed during the 1920's and 1930's. After the acquisition of these concepts, the physical-fundamentals work was much more likely to be successful, since effects at the cell terminals could be analyzed in terms of changes in the physical operation of the electrical circuit elements.

Unfortunately, the Cu_2O cells, which provided most of the experimental evidence during this period, are metal-semiconductor barrier-layer cells. The physical operation of these barriers is much more difficult to analyze than that of p-n junctions, because of the effects of energy levels near the center of the forbidden band gap which are localized at the metal-semiconductor junction. Even today, the operation of such barriers is not wholly understood, especially where the semiconductor is polycrystalline, as was the case in all of the early photocell work. Consequently, the development of really satisfactory physical concepts had to await the p-n junction work of the 1940's which will be dealt with later in this review. However, toward the end of the 1930's a theoretical foundation had been laid which was adequate to provide equations for the I-V characteristics of the cells. The history of the development of the electrical equivalent circuit, and of the electrical barrier theories of Schottky, Frenkel and Joffe, and Mott, is the major emphasis in the following sections of this report.

b. Equivalent Circuit Development: The first attempt at an electrical engineering analysis of Cu_2O cell operation appears to have been done by workers of the Siemens laboratories in Germany; this first analysis was in all essentials the one accepted today. Schottky (32, 59) showed in 1930 that the major part of the potential drop in both rectifiers and photocells occurred at the junction between the metal and the cuprous oxide. Reasoning from this, it was concluded that only those light-generated electrons which crossed this barrier would contribute to the external current of the cell. In Reference (59) this idea was developed to provide a picture of the motion of electrons in the cell structure [Figure 3(a)] providing also a cell equivalent circuit [Figure 3(b)]. Hence, Schottky says (in translation): "If one works without any bias, none of the photoelectrons can contribute to the photocurrent if they are generated within one of the media and are reabsorbed there; this is attributable to reasons of symmetry. However, for photoelectrons which penetrate the boundary layer between the two media, it [the external current] depends on the number of electrons generated in one or the other media, and whether they cross the boundary layer and whether they go into an area with a large, small or zero resistance. If there is no resistance at the boundary, the smallest counter-voltage across the boundary will be enough to counteract this primary current." The equivalent circuit shown by Schottky is completely valid by present-day theories, the nonlinear resistances being shown as diodes in more recent work. The circuit was of the distributed type, as would be necessary to model the Cu_2O back-wall cells of the day, with their rather high oxide resistance. The active element was a current generator with an output proportional to the illumination intensity, which was one of the first points to be experimentally established about these cells.

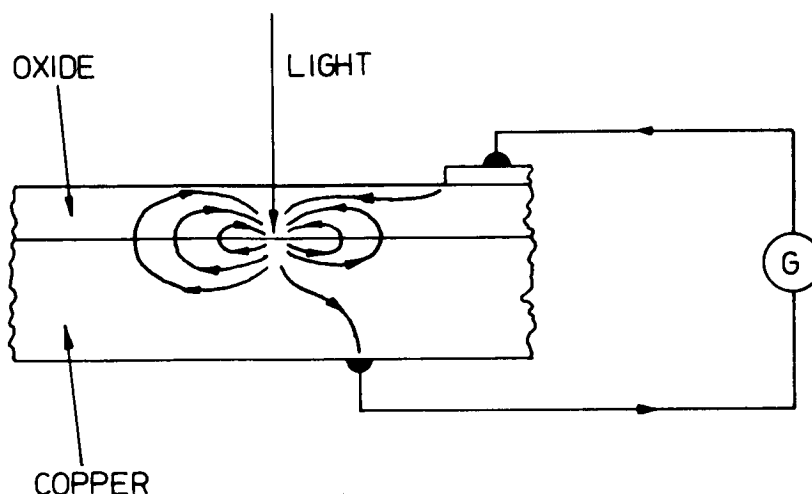


Figure 3(a). Electron flow paths in Cu_2O back-wall cell, after Schottky

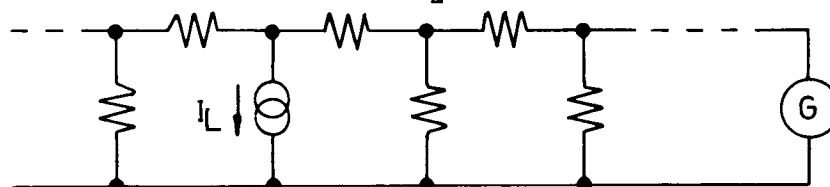


Figure 3(b). Equivalent circuit of Cu_2O cell, after Schottky

Later in the same year (1930), von Auwers and Kerschbaum, also of Siemens, published a particularly complete analysis (38) based on the same ideas as those of Schottky, described above. It was, in particular, shown that the cell was best modelled by a current generator rather than by a voltage generator. The idea that part of the light-generated current which crossed the barrier initially could re-cross it when a bias existed on the barrier due to either external or internal resistances opposing the primary current, was also brought out. The model also provided, at low illumination intensities, an open-circuit voltage proportional to light intensity, as had been established experimentally.

The principal difficulties with the equivalent circuits developed as described above were the values to be assigned to the resistor which is today regarded as a diode, and to that forming the cell series resistance. The diode resistance was certainly known to be nonlinear, but the exact form of the dependence of the resistance on current or voltage was not known. Hence, the form of the dependence of V_{oc} on light intensity at medium and high illumination intensities was not known. The series resistances of the cell were also not known, since in most of the cells made, this resistance arose in the cuprous oxide, which was photoconductive (i.e., exhibited the "inner photoelectric effect" in the terminology of the day).

These difficulties persisted for some years; thus, in 1931 Audubert and Roulleau(64) stated that "in Cu_2O , the photovoltage is proportional to the square root of the illumination intensity...", and Bartlett (65) had to assume a wholly empirical power law for

the variation of photovoltage with illumination intensity. An example of the effect of photoconduction in the cell series resistance is well illustrated by the curves of Figure 4, taken from Reference (66). The curves are for a selenium cell; unfortunately, this method of presenting data was not in general use at the time, and similar curves for Cu_2O cells have not been found. However, statements that the photoconductive effect was seen in photovoltaic cells are to be found. The fact that the illuminated and unilluminated I-V characteristics cross can only be explained by a drop in series resistance for the illuminated cell.

The major success of the equivalent circuit developed by the Siemens workers was that it applied perfectly well to the front-wall Cu_2O cell as it did to the back-wall cell, which was a necessity if it were to be accepted as valid. Thus, the photons absorbed in the oxide caused a current to be generated which passed from oxide to parent-copper for the back-wall cells, and from oxide to counter-electrode for the front-wall cells. The rectifying effect and direction of photovoltage were experimentally found to be reversed in the two cells, and this reversal is necessary from the equivalent circuit.

A further analysis based on the same equivalent circuit was performed by Korosy and Selenyi (66). The main objective of this work was the elucidation of physical principles of operation, but to do this they actually constructed a cell equivalent circuit using a vacuum photocell (i.e., a photocathode device) as the current generator, and a selenium barrier rectifier as the diode: the arrangement is shown in Figure 5. The details of this work are discussed below, but it is interesting to note that the characteristics of the equivalent-circuit model matched those of an actual selenium barrier-layer cell qualitatively, though not quantitatively.

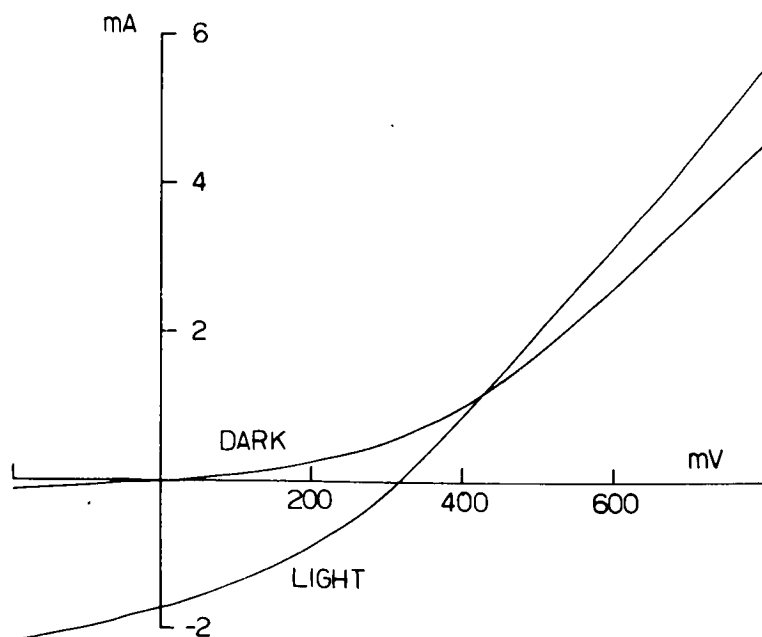


Figure 4. Current-voltage curves of selenium cell, showing the effect of photoconduction, after Korosy and Selenyi

PHOTO-CATHODE
VACUUM TUBE

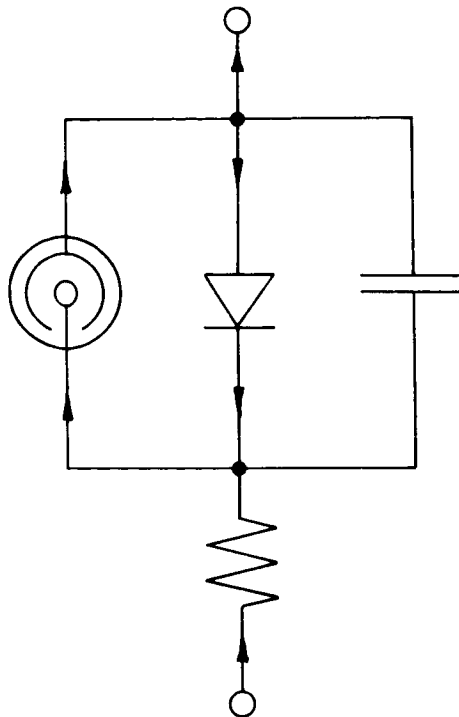


Figure 5. Experimental equivalent circuit of selenium cell,
after Korosy and Selenyi

The equivalent circuits produced by this work were applicable to calculations on the matching of the cell to its load, as well as to physical model analysis. Power-transfer calculations were performed by Wilson (30) and by Bartlett (65), but the primary interest of these analyses was in maximizing the change of power transfer under change of illumination, which is the converse of the requirements for solar cell operation. These calculations were also restricted in their validity to the particular devices considered, since the nonlinear resistor (diode) characteristic was of empirical form.

Except for changes in the physical interpretation of the elements in the equivalent circuits evolved by the Siemens group, the same circuits are in use today for solar cell calculations, and this topic need not be pursued further.

c. Physical Principles of the Fundamental Processes: By the time theoretical work on the photovoltaic effect had got under way, it was established that conduction of electricity in metals (and, it was thought, semiconductors) was by electron motion. Also, work on photoconductive effects made it clear that the absorption of light in photoconductors produced electrons which were free to contribute to conduction in the solid. The other important point which had been well established was the photo-emission effect, and low work-function cathodes had been developed and were in use in photodetectors. The Einstein equation was known to be a valid interpretation,

giving maximum energy possessed by an electron on emission from a surface with work-function W by absorption of a quantum of frequency ν :

$$E_{\max} = h\nu - W \quad (4)$$

and an emitted current proportional to light intensity. Putting $E_{\max} = 0$ gave a threshold for photoemission, photons with energy less than W not causing any current.

A very early theory concerning the photovoltaic effect was that the pressure of photons on the electrons caused the voltage; however, calculation showed that the effect would be much too small to give rise to the voltages observed experimentally.

Following the demonstration by Schottky that a high-resistance barrier existed between the metal and the semiconductor in rectifiers and photocells, many related theories of operation of the photocell were evolved. The similarity between the photoemissive cells and the photovoltaic cells led to a theory of operation in which the photon energy, absorbed by the electron, was used to allow the electron to pass over the barrier between semiconductor and metal [Schottky, 1930, (32)]. This theory of operation covered both front- and back-wall cells, and successfully explained the differences in spectral response and sensitivity. In the back-wall cell, the light arriving at the barrier region had passed through the oxide layer, and thus the high-energy photons were absorbed before reaching the barrier, and did not contribute as much to the cell output as lower-energy photons, which were not so highly absorbed. However, for still lower energies of photons, insufficient energy was imparted to an electron by absorption of the quantum, to allow it to pass over the potential barrier. Thus, the spectral response curve should peak at energies near the optical absorption edge of cuprous oxide, as was found experimentally. In the case of the front-wall cells, however, all photons having energies greater than the minimum necessary to allow the electrons to cross the barrier layer should contribute to cell output, and the spectral response should be a maximum in the energy range where the photons are absorbed near the front surface of the cell, i. e., in the high optical absorption region of cuprous oxide. This was verified experimentally by the work of Auger and Lopicque (46) and Dubar (47), whose experimental results taken together showed most elegantly the correctness of Schottky's theory.

This theory also explained an experimental point which caused considerable confusion when the cuprous oxide cells were first examined. Many workers assumed that the electrons would be emitted from the metal into the oxide, thus passing through the barrier layer in the easy direction of current flow. Several workers expressed surprise at the direction of the current, and so firmly held was this belief that Lange assumed that the back-wall cells operated by photoemission of electrons from the counter-electrode into the oxide.

Schottky's account of the processes occurring in the front- and back-wall cells also explained a phenomenon sometimes observed experimentally. This was a reversal of voltage output for the cells on changing the illumination wavelength. Thus, on illuminating a front-wall cell with light of wavelength near the value at which the back-wall cell response peaked, a potential in a direction corresponding to that for the backwall operation would be seen provided the oxide was thin enough to allow this potential to dominate.

It also is clear from this analysis that a continuous gradation in V_{oc} could be observed as the illumination wavelength varied, but that the effect would be also governed by the details of cell construction. This may be the explanation for some effects observed in experiments which were performed by various workers to detect spectral dependence of V_{oc} . Lange (21) and Korosy and Selenyi (67) expected such a variation by reasoning from the photoemissive effect (Hallwach's effect). It was assumed that the cell voltage was caused by the kinetic energy possessed by the electrons in excess of that needed to pass through the barrier layer, i. e., the open-circuit voltage of a cell illuminated by monochromatic light of energy $(h\nu)$, with a barrier height of W , would be given by:

$$V_{oc} = \frac{(h\nu - W)}{q} \quad (5)$$

Perucca and Deaglio (68) went one step further, and proposed that the operation of the cells was by a true vacuum emission process, rather than the analogous solid-state process proposed by Lange.

So firmly held was this belief in spectral dependence of V_{oc} that when the experiments were inconclusive or negative, reasons for the discrepancy were carefully sought. It is interesting to note that Schottky appears not to have expected this dependence of V_{oc} on photon energy to occur; there is no reference to such an assumption in his published papers, nor did he perform experiments searching for the effect.

Schottky's theory of cell operation was based on the rectifier characteristic. His discussion of the characteristic involved the contact potential difference between the metal and the semiconductor, and when Waibel and Schottky discovered, in 1932 (49) that the rectifier characteristic was dependent on the temperature at which the metal was deposited on the Cu_2O to form the barrier, the authors concluded that the contact potential theory was insufficient to account for the rectifying characteristic. Although the fact that the surface required special preparation before barrier formation had been appreciated from the start of work on Cu_2O rectifiers, it had been assumed that the problem was one of cleanliness, as with measurements of contact potential differences using the vibrating-condenser method. However, the new results indicated that something more than cleanliness was involved, and this is perhaps the first time that it was realized that surface states, as they are now called, also have an influence on electrical properties.

Kurtschatow et al. (55, 56) discussed the theory of operation of the cells advanced by Schottky. Their spectral response measurements confirmed his basic ideas concerning the front- and back-wall Cu_2O cells, but they proposed a small but important difference from the Schottky theory. Schottky considered that only those carriers generated by absorption of light in the region of the barrier layer would contribute to external current. Kurtschatow et al. proposed that the carrier generation by light occurred in the same way in both photoconductive and photovoltaic effects in Cu_2O . This implied a bulk generation of carriers in the semiconductor, which is closer to our present view of cell operation. However, the Soviet workers proposed that the photons need not only energy above a certain threshold value to cause carrier generation, but that in the photovoltaic effect, another increment of energy is necessary to allow the generated carriers to cross the barrier layer. Hence, there should be a difference between the wavelength threshold for photoconduction and that for the photovoltaic effect. To avoid difficulties with front- and back-wall effects in Cu_2O cells, the authors used selenium cells to demonstrate the threshold difference, and they reported finding such an effect. Such an effect would not receive the same explanation today, of course; it may have arisen experimentally because of the particular methods of cell construction that were adopted. The idea of bulk generation of carriers was supported by the experiments of Rupp (52), discussed above, who argued that if the only carrier motion occurred within the barrier region, the effect would have been much smaller than that found because the extremely high fields shown to exist in that region by Schottky would dominate carrier motion and the magnetic field would have had a very small effect.

It appears that Schottky's conception of events taking place in the cell had meanwhile been modified, since in 1932 (69) he remarked on the ability of the generated carriers to penetrate to the barrier from their place of generation within the semiconductor bulk. In other words, it was clearly appreciated that the diffusion length of the carriers could be orders of magnitude larger than their mean free path. His reported measured quantum efficiency of 25 to 50% also supported the concept of one carrier being generated by each photon.

At this stage of development, an acceptable qualitative picture of cell operation had been built up, but because of a lack of a satisfactory analysis of the forward characteristic of the rectifier effect, a valid quantitative concept of cell operation was still lacking. An attempt to overcome this deficiency was made by Frenkel and Joffé. Their series of publications started in 1930 with a rectifier analysis (70), but the first consideration of the photovoltaic effect appeared in 1932 (71, 72). The model analyzed was based on the work of Schottky, with a narrow barrier separating regions of differing electron concentration. The motion of electrons through the barrier was analyzed by means of wave mechanics, the width of the barrier being small enough to permit 'tunneling' of electrons through the potential hill, rather than requiring them to have sufficient energy to pass over the top. For the photoelectric case, a metal-semiconductor contact was considered, with a high density of free electrons in

the metal and a comparatively low density of free electrons in the semiconductor. The free electron density (n) in the semiconductor was taken to be:

$$n = N \exp \left(- \frac{\epsilon}{kT} \right) \quad (6)$$

with ϵ about 0.3 eV and N between 6×10^{17} and $2.5 \times 10^{19} \text{ cm}^{-3}$. Initial analyses were valid only for $n \ll N$, i.e., for values of applied bias small compared with (kT). In Reference (72), a more exact analysis was performed for larger bias values, and the results obtained were

$$J = J_0 \left[1 - \exp \left(\frac{qV}{kT} \right) \right] \quad (7)$$

where J = current density,
 V = applied bias, and
 q = electronic charge.

An expression for J_0 was derived from assumptions which are not accepted today, and the analysis relating to J_0 was further complicated by an attempt to include the experimental fact that the reverse characteristic of rectifiers did not saturate at J_0 , but showed leakage and breakdown effects. In accounting for the nonsaturation in reverse current, an equation was derived of the form:

$$J = J_0 \left[1 - \exp \left(\frac{qV}{kT} \right) \right] \exp (\beta |qV|) \quad (8)$$

with $\beta \approx 1.5$.

This was based on a voltage-dependence of 'the transparency coefficient' for the junction, whereas Eq. (7) was derived assuming this coefficient to be independent of bias voltage.

However, the expression obtained for J_0 did show a rapid variation with temperature, which explained the observed fact that rectification disappears at high temperatures.

However, the main importance of the work lay in the derivation of Eq. (7). Here was the needed forward characteristic of the rectifier, which allowed the open-circuit voltage expression to be derived:

$$J_L = J_0 \left[\exp \left(\frac{V_{oc}}{kT} \right) - 1 \right] \quad (9)$$

For the case of low values of V_{oc} this reduced to

$$V_{oc} = \frac{kT}{J_o} \times J_L \quad (10)$$

where J_L = light-generated current.

Another topic analyzed by Frenkel and Joffé was the threshold wavelengths for photoconductivity and the photovoltaic effect, but this work is based on premises which are not now regarded as valid, mainly because the experimental effects which the authors attempted to analyze would now not be regarded as fundamental.

The above analysis is based on a fundamentally incorrect model, as was shown later by various workers. However, the exponential dependence of V on illumination intensity, arising from the use of Maxwellian statistics, is a fundamental point which is correct, and which forms a part of later theories.

Also in 1932, Teichmann published a paper (73) in which a novel explanation was offered for the rectifier effect. By analogy with the laws of gas dynamics, a "field funnel" was postulated to act on the electrons passing through the barrier.

The geometry of the concept is illustrated in Figure (6). The divergent electric field was thought to arise from the juxtaposition of two crystal lattices (copper and Cu_2O) with different unit cell dimensions. The concept was not widely accepted, and was ultimately shown to be invalid by Fink and Adler in 1940 (12).

Yet another theory concerning the structure of the metal- Cu_2O interface was propounded by Lange in 1933 (74). It was well known that the surface treatment of the Cu_2O was critical for the successful operation of the cells, an "activation" step before deposition of the counter-electrode being necessary for development of good sensitivity in the cells. Lange also found a photovoltaic effect to be present even in some cells in which the rectifying characteristic asymmetry was absent. Hence, it was proposed that the rectifying effect of the metal Cu_2O contact was quite separate and had no bearing on the fundamental mechanism of cell operation. Instead, a chemically activated surface layer on the oxide was proposed, and only those photons absorbed in this layer were thought to contribute to cell output. This theory is partially a reiteration of Schottky's postulate of the existence of a high-resistance layer of stoichiometric Cu_2O at the barrier layer. This region of low acceptor concentration is believed to exist in present-day theories of cuprous oxide rectification, and gives rise to the Mott type of barrier structure, as discussed below. The experiments of Lange were done using chemical reduction processes to activate the oxide surface, and this would certainly produce a low-acceptor density region near the oxide surface.

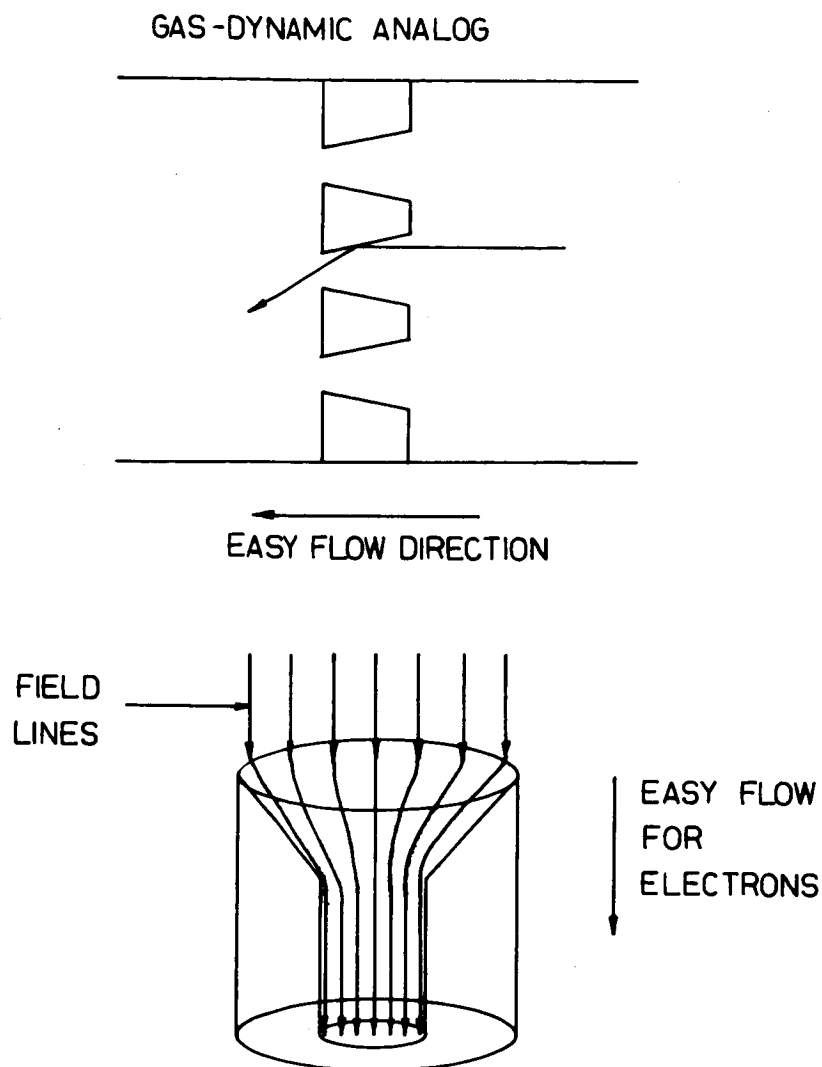


Figure 6. 'Field-funnel' concept of Teichmann, for explanation of the rectifier effect

Lange notes that chemical analysis methods would not be capable of proving or disproving the theory because of the very small quantities of material in the thin surface layer, and the fact that very small departures from stoichiometry could have large effects on the electrical properties of the layers. The attempt to separate the rectification and photovoltaic effects appears to have some validity also. As discussed above, the chemical reduction treatment would probably produce an acceptor concentration gradient in the oxide surface. This would give rise to small displacements of the Fermi level relative to the conduction band in the region of the oxide surface, which would produce correspondingly small photo-emfs. Thus, the results seen by Lange may have been more akin to Dember photovoltages (see the section below on Dember effects).

The equations developed by Frenkel and Joffé were examined for validity with experimental results obtained on selenium barrier-layer cells by Barnard (26). The major point which arose from this work concerned the value of β in Eq. (8). Barnard found a value of about 15 to fit the experimental facts best, but he also found that β was a function of the fraction of the cell area illuminated, reaching the 1.5 value derived by Frenkel and Joffé at vanishingly small illuminated areas. The actual value to be assigned to β was shown to vary widely with the detail of the contact band structure, and the presence of localized levels at the barrier. Theoretical analysis of this point was difficult because assumptions had to be made which did not fit all experimental cases. However, the equations derived by Frenkel and Joffé were partially validated by the work of Barnard, whose analysis of the reasons for deviation from the theory were also significant. The β values observed were ascribed to space-charge limitation of current when the whole cell area was illuminated, an effect which would be absent in the limiting case when the illumination area tended to zero, corresponding to the one-dimensional analysis of Frenkel and Joffé.

Another contribution to the barrier photovoltaic effect theory during this pre-1940 period was made by Mott in 1939 (75, 76). Mott points out that the theories of rectification developed by Frenkel and others assume that the cuprous oxide conducts by containing free electrons. However, Hall effect measurements showed that the current carriers were actually holes, and in this case the theories give incorrectly the direction of rectification. Mott's main contribution was to reconsider the energy band structure at the barrier, and his conclusions coincide with present-day concepts, as shown in Figure 7. The barrier width was taken to be of the order 10^{-4} cm, in agreement with the measured values of Schottky and Deutschmann (35), rather than the 10^{-7} cm which had been assumed by Frenkel. Thus, the electron passage through the junction was by carriers having energy sufficient to surmount the barrier rather than by tunneling as analyzed by Frenkel. By conceptually bringing a metal into contact with a semiconductor, Mott showed that a space-charge region would be established at equilibrium. This would produce a field in the junction region in the correct direction both to explain the rectification direction and the barrier photo-emf direction, and to show that these are of necessity linked in such a way that the light-generated current passes through the junction in the high-resistance direction, the point which had given the experimentalists such difficulty at the start of work on Cu_2O rectifier photocells. For a barrier layer of the thickness considered by Mott, the carrier passage through the junction was partly governed by diffusion processes. The current-voltage relationship derived was

$$J = \frac{V_o - V}{\rho_\infty} \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] \quad (11)$$

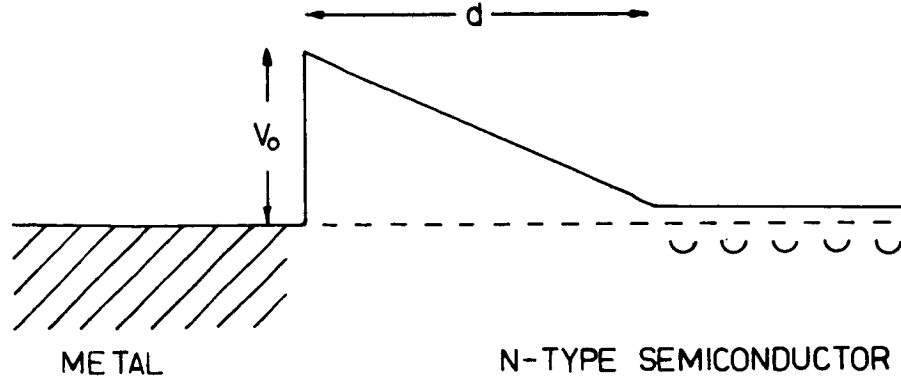


Figure 7(a). Energy band diagram of rectifier, after Mott

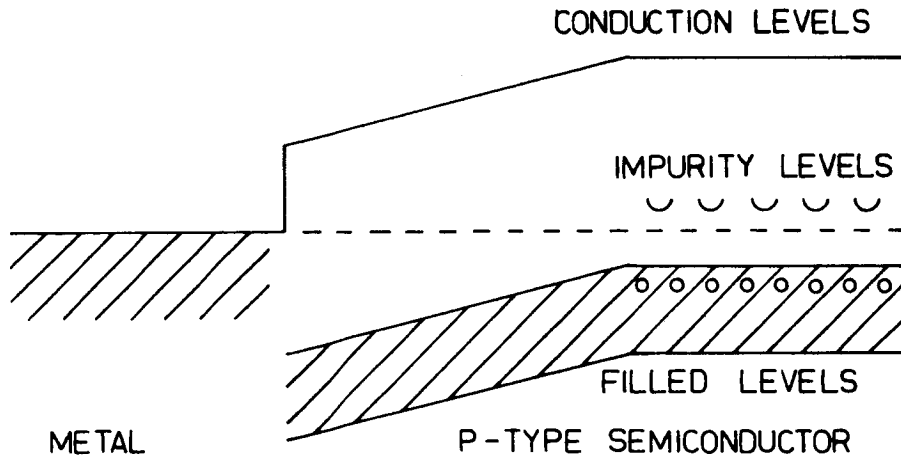


Figure 7(b). Energy band diagram of Cu_2O photocell, after Mott

where V_0 = barrier height as shown in Figure 7, and ϕ_∞ = limiting reverse resistance. This differs from Eq. (8) of Frenkel, but once again the rectifier operation is governed by the exponential term in $\left(\frac{qV}{kT}\right)$ which arises from the use of a Maxwell distribution function for the occupation of energy levels in the semiconductor.

Equation (11) is valid only for the particular barrier structure visualized by Mott, in which a variation of the impurity distribution near the junction is present such that a thin layer with low impurity density is adjacent to the metal. This thin layer makes an abrupt junction with the semiconductor bulk which has a much higher impurity concentration. If the metal-semiconductor barrier is high (large value of V_0 in Figure 7), the junction width (d in Figure 7) is independent of applied bias.

Mott's theory described a device having no space charge in the barrier layer. This approximation is not wholly valid, and Schottky provided an analysis dealing with two cases nearer the experimental facts:

- (i) A device in which all carrier-generating species in the space-charge region are ionized ("exhaustion layer"), and
- (ii) a device in which the ionization is incomplete.

In common with Mott, Schottky assumed a barrier region 10^{-4} to 10^{-5} cm thick, in which a current carrier would experience multiple scattering events as it passed through the junction. Both theories were based on a free-carrier diffusion process, and in the case of an "exhaustion" layer, essentially the same results were obtained in both theories with an exponential dependence of current on applied voltage.

Thus, the work of Mott and Schottky laid the foundations for the presently accepted theories of p-n junctions. Both theories accounted satisfactorily for the junction width, the I-V characteristic, and its behavior under temperature changes. The I-V characteristic is of the form:

$$J = J_0 (\exp \alpha V - 1) \quad (12)$$

and was called the 'rectifier equation' in the terminology of the period, but is now known as the 'diode equation'. The differences between these theories and later ones are concerned with details of the band structure and charge distribution in the barrier layer. These differences give rise to differing values of J_0 , and discussion of this highly interesting parameter is postponed to later sections of this report.

d. Summary: The development of presently accepted theories of operation of barrier photovoltaic devices can be summarized as follows:

- (1) Points established by Schottky in 1930
 - A barrier layer exists between metal and semiconductor, and the main potential drop occurs across this during rectifier operation.
 - Photocurrent generation is intimately connected with the region in which the barrier layer is situated.
 - The cell equivalent circuit contains a current generator whose output is proportional to illuminated intensity.
- (2) In 1932, Frenkel and Joffe¹ analyzed the rectifier characteristic, showing an exponential dependence of I on V arising from the Maxwellian distribution of electron energies.

- (3) In 1939, Mott proposed an energy band diagram for the rectifier and photocell, and an analysis of this band model. This analysis was reworked by Schottky to include ionization in the space-charge region, and this work of Mott and Schottky provides the basis of the presently accepted theories of p-n junction behavior, for application to Cu_2O devices.

D. THE DEMBER EFFECT

1. Introduction

Whenever a nonuniform distribution of charge carriers of both signs (holes and electrons) exists and the mobilities of the two types of charge carriers are different, diffusion currents occur which cause an equalizing electric field to be set up. Such an effect occurs at an illuminated metal-semiconductor contact at which no potential barrier exists, in the semiconductor bulk under conditions of nonuniform illumination or nonuniform absorption near a semiconductor surface when surface recombination is present, and under any generally nonuniform excitation condition. The effect at a metal-semiconductor interface is called the Dember effect, after its discoverer; similarly, potentials having their origin in the diffusion process are generally called Dember potentials. The discussion given here will be concerned with photostimulated diffusion potentials and not only the specific case of a metal-semiconductor interface.

2. Discovery and Experimental Work

The discovery of the effect is usually attributed to H. Dember, who published two papers in 1931 (77, 78) describing the results of his studies on cuprite (Cu_2O) and other minerals. Approximately seven years earlier W. W. Coblentz (79) published the results of some studies on Molybdenite (MoS_2) in which he had observed and studied the generation of a photo-emf under conditions of nonuniform illumination. Coblentz had previously studied photoconductivity in molybdenite samples but, at the suggestion of T. W. Case who had observed a photo-emf in his own studies, began to study the "Actinoelectric" properties of the material in 1922.

Coblentz used soldered copper electrodes on his MoS_2 samples and focused the light on areas away from the electrodes. His light source consisted of a ribbon filament tungsten lamp, and a water filter was used to prevent heating of the sample. He found that several localized areas of the crystal produced much stronger responses than the rest of the crystal and that the response reached its peak value "instantaneously" (time short with respect to the response time of the galvanometer). Using a monochromator he investigated the spectral response of the effect and found that the maximum response occurred between 0.2 micron and 0.9 micron with no response beyond 1 micron. It was also noted that the spectral distribution of the photo-emf did not coincide with that of the photoconductivity. Although numerous studies were made, including the effects of intensity and temperature, no explanation for the origin of the observed effect was offered. It was not until Dember's work in 1931 that a reasonable explanation was put forward.

In the first (77) of two papers published in 1931, H. Dember reported the results of his studies on some large uniform crystals of cuprite (Cu_2O). In his first experiment an octahedral crystal was mounted between two brass electrodes such that it could be rotated and illuminated from various angles. The light source consisted of a 500-watt mercury lamp at a distance of 30 cm from the sample. When the crystal was illuminated in the vicinity of one electrode voltages as high as 0.15 V were observed. When the opposite electrode was illuminated the photo-emf reversed its direction. The author attributed the effect to the direct nonuniform illumination of the boundary between the electrode and the crystal.

A second experiment consisted of contacting a large crystal in such a way that the electrodes were completely shielded from the illumination, and illuminating the specimen from different angles. An emf having one direction occurred when the crystal was illuminated on one face. When the crystal was rotated 110° to illuminate another facet the direction of the photo-emf was reversed. As a result of this and similar experiments it was concluded that the direction of the photo-emf was a function of the direction of illumination.

Other experiments with shielded and ring type electrodes were performed to show that it was not a barrier layer, as in the case of Schottky's photocells, that was determining the direction of the emf. It was finally concluded that the generation of a photo-emf inside a crystal could occur only when the incident light caused the emission of free electrons which could diffuse into the crystal. At the point where the light entered the crystal the electron concentration was greatest, decreasing along the path of the light into the bulk of the crystal. This concentration gradient caused the electrons to diffuse in the direction of the light.

The second paper (78), published in 1931, reported results from similar experiments using different specimens. These included cuprite samples from various countries and a sample of Chinese Proustos (Ag_3AsS_3). The effects of varying the intensity, on the photo-emf and current flux were investigated. A rotating disc was used to vary the intensity. The current was found to vary linearly, while the voltage variation appeared logarithmic in nature. The idea that the photo-emf was caused by a gradient in the concentration of the photogenerated electrons was reiterated. In addition, Dember stated that the light pressure acted on the electrons in the same direction, thus enhancing the effect.

In two papers published in the following year (80, 81), Dember continued his studies on other materials and made further attempts to establish the difference between his "crystal-effect" and Schottky's barrier effect. To this end he illuminated a Cu_2O single crystal plate through platinum nets isolated from the crystal by air or glass plates to prevent the flow of electrons into an external circuit. Under illumination a potential difference between the two sides was detected. Dember then concluded that the photo-voltaic barrier explanation did not apply in this case and that the photoelectrons were displaced in the direction of the light by light pressure.

Also in 1932, L. Bergmann published two papers (63, 82) dealing with photo-emfs under intermittent illumination. The intermittent signal was fed to an amplifier and detected by a telephone and in some cases a milliammeter. Signals were detected not only in known photovoltaic structures such as Se-Fe and Cu_2O -Cu rectifiers with metallic contacts but also with iodine, mercury iodide, and CdS powers insulated from the fixture by glass plates. The effect was measured under all possible combinations of illumination, both intermittent and continuous, and on a single side or both sides simultaneously. The effect was cancelled when synchronized illumination was used on both sides but doubled when the sides were illuminated 180° out of phase. Bergmann saw a connection between his observations and the Dember effect and believed that the same mechanism was operative in his specimens.

Four years later, in 1936, Bergmann published the results of an exhaustive study of the photoeffect in some 76 compounds using the above technique (62). In some materials the direction of the photo-emf was dependent on the wavelength of the light source. A satisfactory explanation for the effect was still lacking; however, it was still felt to be related to the Dember effect and was believed to result from several effects connected with light absorption in these materials. Since the samples were naturally occurring minerals with many flaws and impurities these results are not surprising.

3. Development of the Theory

The first attempts to develop a mathematical theory for the diffusion or Dember potential seem to have been made by J. Frenkel. In a letter published in 1933 (83), discussing the motion of holes and electrons in the presence of trapping, he developed the following expression for the Dember potential

$$\varphi = \frac{kT}{q} \frac{\mu_n - \mu_p}{\mu_n + \mu_p} \ln \frac{N_o}{N} \quad (13)$$

where μ_p and μ_n were the mobilities of the holes and electrons, and N_o and N were the carrier concentrations in the illuminated and unilluminated regions. As Frenkel observed, this is the correct expression for the case of high-intensity illumination. It can be seen from the equation that if the two mobilities are equal there will be no potential. The expression for the potential was derived by solving the continuity equation under the conditions that the sample is illuminated along one plane only and that the electric field does not vary with the x coordinate. Frenkel pointed out that it is possible, in principle, to determine the ratio of the hole and electron mobilities from the above equation.

In Frenkel's second paper on the subject (84), published in 1935, a much more detailed mathematical treatment was given. In this paper he attempted to develop an elementary

theory of both the Dember effect and the Kikoin-Nisov effect (a photo-magneto-electric effect) in semiconducting solids. Assuming that the velocity distribution of the photo-generated carriers was Maxwellian, fundamental equations for rate of change of hole and electron concentrations with respect to time were developed, by using the particle conservation concept. By combining these equations with Poisson's equations, expressions were obtained for the Dember potential under conditions of weak and strong illumination. The analysis of the high-intensity illumination case was marred by the assumption that an approximation used to obtain a linear relation between illumination and carrier generation for weak illumination was also valid in the high-intensity case, in obvious contradiction of his preceding development. He again obtains substantially correct expressions for the Dember potential in the two extreme cases.

Noting the flows in the work of Frenkel and others, Landau and Lifschitz in 1936 produced another extensive study (85) which included the effects of contact potentials and the variation of the velocity distribution of the freed carriers from the Maxwellian distribution. It was shown that a photo-emf could exist only if carriers of both types (holes and electrons) were generated and have different mobilities or, in the case where only carriers of one sign are present, if the velocity distribution of the carriers is non-Maxwellian. An accurate calculation of the velocity distribution function indicated that the magnitude of observed Dember potentials is too great to be attributed to the variation of the velocity distribution from that of Maxwell. The analysis of the contact potential change under illumination indicated that this effect may completely compensate the diffusion potential or even change the sign of the observed photo-emf. The following general expression was obtained for the combined Dember effect and contact potential:

$$V = \frac{kT}{q} \left[\frac{1-X}{1+X} \ln \left(1 + \frac{C}{C_1} \right) - \ln \left(1 + \frac{C}{C_2} \right) \right] \quad (14)$$

where C_1 and C_2 are proportional to the number of electrons in an unilluminated unit volume, C is the photogenerated charge density and X can be related to the ratio of the mobilities of the charge carriers. The first term on the right side of the equation is the voltage due to diffusion; the second term is due to the contact potential changes. This reduces the Frenkel expression for the case of high-intensity illumination if one ignores, as Frenkel did, the contact potential.

In 1938 B. Davydov published his paper on the Dember effect (86). With relatively simple calculations he was able to show, as had Landau and Lifschitz previously, that in the case of a single type of charge carrier no photo-emf could be detected unless the velocity distribution of the free carriers were non-Maxwellian and that the potentials caused by this effect would be small compared with those observed experimentally. This indicated, as had the work of Landau and Lifschitz, that the observed effects were due to the existence and diffusion of free charges of both signs.

Davydov's analysis of the Dember potential covered the case of weak illumination only and included the effects of the contact potential. The analysis neglected variations in the charge carrier transmission coefficient with contact potential. The results did not agree with those of Landau and Lifschitz for the low-intensity case. Davydov points out that these workers made several improper approximations and that, consequently, their results were valid only in the case of high contact resistances.

4. Summary

The concepts finally settled on by the investigators of the 1930's are essentially those held today, and the mathematical expressions developed for the bulk diffusion potential are essentially correct. An analytical discussion of the Dember effect at a metal-semiconductor interface (no barrier) is much more difficult and no such discussion has been found in the period preceding 1940. There is some question whether this effect is understood in general even today.

The Dember effects do not appear to hold much promise in the field of energy conversion. The magnitude of the power produced by this effect is extremely small in comparison with that produced by barrier-type devices for a given light source. The maximum open-circuit voltage under strong illumination is, in principle, the same but the short-circuit current of the barrier photocells is generally much larger. This is because the carriers generated in or near the barrier are accelerated fairly rapidly by the strong field and, thus, are afforded little time for recombination of this region. In the bulk or diffusion photoeffect no such rapid removal occurs and the consequent recombination diminishes the short-circuit current. Computations based on typical values for germanium indicate that the current associated with the diffusion potential will be, at best, approximately one tenth that of a barrier photocell.

There is one situation in which the Dember or diffusion effect can be more efficient than a barrier-type photocell. If the radiation is not strongly absorbed by the cell, as in the case of high energy radiation, it is possible for the diffusion effect to be the more efficient.

Because of the low efficiency there is little current interest in the Dember effect, although it has been proposed as a possible explanation for the high-voltage photovoltaic effect in some materials.

**III. THE DEVELOPMENT OF PRACTICAL
ENERGY CONVERSION DEVICES (1940-1955)**

III. 1940-1955
DEVELOPMENT

GLOSSARY OF SYMBOLS FOR SECTION III

A	empirical constant in the diode equation	I_p	current arising from hole motion	p_o	excess hole concentration in n region
b	ratio of electron to hole mobility	I_{no}	reverse saturation current arising from electron motion	p_p	hole concentration in p region
d	effective thickness of barrier layer	I_{po}	reverse saturation current arising from hole motion	P	power
d_t	spatial coordinate of front surface of semiconductor	I_o	reverse saturation current	q	electronic charge
d_r	spatial coordinate of back surface of semiconductor	I_{sc}	short-circuit current	Q	quantum efficiency
D_n	diffusion constant for electrons	J	current density or illumination intensity, in context	R_L	load resistance
D_p	diffusion constant for holes	J_o	reverse saturation current density	R'_L	maximum power load resistance
E_c	energy at bottom edge of conduction band	k	Boltzmann's constant	R_o	zero-point diode resistance
E_f	Fermi level energy	L_n	diffusion length for electrons in p region	R_s	series resistance
E_{fn}	Fermi energy on n-type side of pn junction, or quasi-Fermi level energy for electrons, in context	L_p	diffusion length for holes in n region	R_{sh}	shunt resistance
E_{fp}	Fermi energy on p-type side of pn junction, or quasi-Fermi level energy for holes, in context	m^*	effective mass of electrons or holes	T	absolute temperature
E_g	width of forbidden bandgap	n	electron or hole density, or free electron density in extrinsic semiconductor material, in context	V	voltage
E_o	energy level defined for surface state studies	n_d	electron density at $x = d$	V_o	barrier height
E_v	energy at upper edge of valence band	n_i	free electron density in intrinsic semiconductor material	V_{oc}	open-circuit voltage
F	absolute value of field intensity at $x = 0$	n_n	electron concentration in n region	x	spatial coordinate
g_o	rate of hole generation at $x = 0$	n_o	excess electron concentration in p region, or electron concentration at $x = 0$, in context	x_a, x_b	spatial coordinates of points sufficiently far from pn junction that minority carrier densities are unaltered by conduction through junction
g_p	rate of thermal generation of holes in n region	n_p	equilibrium electron concentration in p region	x_{Tn}	edge of transition region
$g(x)$	rate of hole generation by light absorption in n region (function of position)	n_{po}	unilluminated free electron density	α	optical absorption constant, or constant, in context
h	Planck's constant	N	density of donors or acceptors	β	number of electrons released per photon absorbed
H_s	incident photon flux	N_a	acceptor density	ΔE	energy difference
I	current	N_d	donor density	Δn_p	excess electron density under illumination
I_D	diode current	p	free hole density in extrinsic semiconductor material	η	conversion efficiency
I_L	light-generated current	p_n	equilibrium hole concentration in n region	κ	dielectric constant
I_n	current arising from electron motion			μ_n	electron mobility
				μ_p	hole mobility
				ν	frequency, or constant, as indicated in context
				σ_n	conductivity of n-type material
				σ_p	conductivity of p-type material
				τ	minority carrier lifetime
				ψ	electrostatic potential energy

III. THE DEVELOPMENT OF PRACTICAL ENERGY CONVERSION DEVICES (1940-1955)

A. INTRODUCTION

As described in Section II, the progress made before 1940 concerned devices made mainly with copper oxide or selenium, and these were intended for detection purposes rather than energy conversion. However, the experimental work had provided enough background that the fundamentals of semiconductor theory and photovoltaic effect analysis could also be established. During the late 1930's and early 1940's, the need for microwave mixer and detector diodes for radar equipment provided a great stimulus for experimental work on silicon, and also created an active interest in the development of a theory to permit analysis of semiconductor point-contact diodes made of this material. The resulting cooperative effort between industrial laboratories and academic institutions, coordinated by the M.I.T. Radiation Laboratory, produced great progress in the materials technology of silicon, and advances in the theory of semiconductor and rectifier properties.

Building on the earlier theoretical work, and from the experimental measurements made on germanium and silicon devices, Shockley developed the diffusion theory of p-n junction rectification and transistor theory, which has been most widely used for device analysis. The technology advances made during the early 1940's were extended to allow development of the transistor as a practical device, which in turn prompted an intensified program of semiconductor research. This ultimately provided the materials technology for growing large single crystals of silicon, and the solid-state diffusion process, which were combined to produce the first practical solar cell in 1954.

During the 1950's, compound semiconductors began to receive attention again, after the earlier work of the 1930's had been overshadowed by the results with silicon and germanium. Thus, almost simultaneously with the announcement of the silicon solar cell, Reynolds obtained good energy conversion efficiency with the CdS solar cell, and early reports of photovoltaic measurements on III-V semiconductor compounds also began to appear.

During the years 1940-1955, therefore, a very large research and development effort on semiconductors resulted, among others, in the development of practical energy conversion devices. This section is devoted to an account of the advances made during this period.

B. MATERIALS TECHNOLOGY

1. Introduction

The development of today's highly sophisticated semiconductor device industry can be traced directly to the tremendous advances in materials technology which occurred, for the most part, in the decade or two following the late 1930's. It was during this period that the materials purification and crystal growth techniques were developed which made possible the transistor and the myriad of related devices. The development of these techniques was coincident with an intensive study of the properties of semiconducting materials and of the effects of various impurities on these properties. The major effort was concentrated on germanium and silicon. These studies, combined with the development of impurity diffusion processes in semiconductors, provided the necessary background for the controlled formation of the p-n junction, the essential part of the majority of semiconductor devices, including the present day solar cells. The experimental investigations were often paralleled by, and also in many instances stimulated, a strong theoretical interest in semiconductor phenomena which led to an increased understanding of the physics of semiconductors and provided a feedback for further experimental work. A brief discussion of this early development is necessary to any historical survey on the development of photovoltaic cells; indeed, it was during these early investigations of crystal growth and materials properties that the p-n junction photovoltaic effect in silicon was inadvertently discovered (87-89).

2. Material Purification, Crystal Growth, and Semiconductor Properties

a. Elemental Semiconductors: One of the more positive effects of World War II was to provide a jolting stimulus to the field of semiconductor physics. The impetus was supplied in the form of contracts under the sponsorship of the National Defense Research Committee (NDRC) to a number of universities and commercial laboratories in the United States (90). The motive for this interest was the development of crystal rectifiers and crystal mixers for radar applications. Prior to the war the field of single crystal-semiconductor technology was relatively dormant. Available materials were not highly refined, many of the properties of the materials were not generally understood, and applications for semiconducting materials were few. The major application for germanium appears to have been as a thin-film resistor (evaporated on glass) in electric circuits, although the rectifying properties of germanium-metal point-contacts were well known. Silicon was used in the fabrication of point-contact rectifiers for microwave detectors in laboratory studies. The war-time needs, both in the United States and England and in Germany, caused a dramatic change.

The first requirement for producing semiconducting devices with predictable and controllable properties is a source of relatively pure material. During the early work at Bell Laboratories around 1940 (Reference 90, p. 311), the normal impurity segregation which takes place with crystal growth by the Bridgman technique was used to purify the then available silicon. This silicon was commercial electromet material with a purity

of 99.8%. The growth procedure resulted in ingots approximately 4 1/2 in. long and 1 5/8 in. in diameter of which the bottom 2 in. were discarded.

During the period 1940-1944 the DuPont Company developed a technique which produced, consistently and uniformly, silicon of purity better than 99.9%.

The essential part of the technique was a reaction chamber process utilizing the zinc reduction of silicon tetrachloride by zinc vapor. The reaction was carried out at a temperature such that the zinc, zinc chloride, and excess silicon tetrachloride were carried off in the form of vapor, while the pure silicon remained in the reaction chamber in the form of crystals. After removal from the chamber the silicon was leached in hydrochloric acid and rinsed in distilled water.

A similar method was used by DuPont to produce high-purity germanium. A second method used for the purification of germanium by H.Q. North of General Electric was the reduction of germanium oxide by hydrogen. Ingots grown with these materials were sufficient for the fabrication of rectifiers, and while tolerating wide production distributions and low yields, it was often not necessary to discard portions of the ingots because of impurities. The precise measurement of physical properties, and the development of sophisticated devices as well as of economical production processes, however, required materials of greater purity (better than 1 part in 10^8 or less) than these processes could provide.

It was not until the early 1950's, which saw the introduction of the zone refining process (91) and later the floating zone technique for silicon of Keck and Golay (92), that germanium and silicon of this purity became available. These zone purification techniques consist of melting a narrow region or "zone" of the crystal and then moving this region along the length of the crystal, carrying along with it the impurities which are rejected in the re-freezing process and which are deposited at the end of the crystal, which portion can then be discarded. The reason for the segregation of the impurities is their lower solubility in the solid phase of the semiconductor than in the liquid. Some of the moving zone techniques were later adapted for growing single-crystal ingots both of germanium and silicon.

Methods for the growth of large single crystals of many organic and inorganic materials have been known since the middle of the nineteenth century. Most of the early work was concerned with growth from a solution, but melt-growth techniques, such as those of Bridgman (93) and Czochralski (94), had been developed for the growth of metals, approximately two decades before World War II. These techniques, with modifications, were finally settled on for the growth of silicon and germanium ingots. During the early work at Bell Laboratories, performed under NDRC contract, silicon ingots were grown by simply heating a large mass of silicon to a temperature well above its melting point and then allowing it to cool slowly (88, 89). Due to the impurity segregation process in freezing, a gradient in purity existed from the outer surface to the core of the ingot. Ingots grown in this fashion were generally cracked because of the anomalous negative

expansion coefficient of the material upon freezing, which causes the central portion of the ingot, which is the last to solidify, to break its confinement. The cracking was highly undesirable, so that other techniques were sought. A process which successfully eliminated the cracking was to heat the material in the normal manner but, instead of allowing the material to cool by slowly reducing the power supplied to the furnace, the material was slowly withdrawn from the furnace which was maintained at a constant temperature. This was an adaptation of the Bridgman method. The ingots produced were relatively crack-free, with an impurity gradient from top to bottom. In the early silicon ingots produced at Bell Laboratories the upper half of the ingot exhibited p-type conductivity, while the lower half was n-type. It was during experiments with rods and plates cut from sections of such ingots that the p-n junction photovoltaic effect in silicon was discovered in 1941 (88, 89).

The techniques used to grow germanium ingots during the early and mid 1940's were essentially the same as those used to prepare silicon crystals. They normally consisted of variants of the Bridgman method insofar as either the tube containing the melt was slowly removed from the furnace or the furnace itself was physically raised to expose the tube. The material produced was satisfactory for point-contact rectifier uses, although a large amount of waste was incurred and the material was probably highly polycrystalline since the technique of "necking" the tube so that only one crystal will act as a seed to the melt appears to have not yet been used. Crystals of germanium grown in this manner occasionally contained regions of n-type and p-type conductivity, similar to those found in silicon and it was discovered, around 1944, that the boundaries of such regions exhibited photovoltaic sensitivity (95, 96). The electrical properties of the germanium could be altered by the addition of small amounts of impurities, such as antimony and arsenic, to the melt.

The properties of the silicon ingots could be controlled to some extent by the same process. However, because of its highly reactive nature, silicon tended to become contaminated by whatever material was used as a crucible, making its properties more difficult to control than those of germanium. In the late 1940's and early 1950's after the introduction of the Czochralski or "crystal pulling" techniques for the production of silicon and germanium ingots, the method of adding impurities to the melt during crystal growth was used to prepare p-n junctions (97). In general, the Czochralski method has been found to produce crystals with a lower defect density than other known techniques, and to provide sufficient control of impurity concentrations, so that this technique has become the one generally used for the production of crystals for solar cell fabrication.

The necessity for controlling the electrical characteristics of the semiconductors led to an extensive study of the properties of the materials and the effects of impurities on these properties. Particularly, the effects of boron and phosphorus on the conductivity type and resistivity of silicon were explored in the 1940's by Scaff et al (88, 98). They determined that boron and other group III elements caused the material to exhibit p-type conductivity, while the addition of phosphorus, arsenic, and other group V elements resulted in n-type conductivity. Compensation effects were also noted. Extensive

measurements of resistivity and Hall effect as a function of temperature on silicon samples containing from 0.0005 to 1.0 percent boron or phosphorus were reported by Pearson and Bardeen (99). Similar studies were performed on germanium by Lark-Horowitz and Johnson. Most of this early work was performed during World War II under the NDRC and was described rather thoroughly by Torrey and Whitmer (90).

In the early 1950's the results of numerous detailed studies of impurity effects on the properties of silicon and germanium began to appear in the published literature. Experimental studies of solubilities, impurity distributions, diffusion coefficients, ionization coefficients, ionization energies, and capture cross sections covering a wide range of elements were published. J.A. Burton's paper (100) provides a good review and bibliography of this work, much of which occurred at the Bell Laboratories. The theoretical work of Burton (101), Pfann (91), and others laid the basis for understanding and predicting the behavior of impurities during crystal growth and zone purification. All of this work provided the foundation for the production of crystals with highly controlled and well-known impurity concentrations whose electrical and optical properties could be studied with confidence. Investigators such as Prince (102, 103) and Burton (104) of Bell Laboratories studied the effects of impurity concentration on mobility and lifetime, while others such as Dash and Newman (105) of General Electric studied optical absorption. As a result of these and many other investigations the general understanding of semiconductor properties was increased dramatically during the early 1950's, at least as far as elemental semiconductors were concerned.

b. Compound Semiconductors: There was no burst of interest in the compound semiconductors during the 1940's corresponding to that which occurred for silicon and germanium. These elemental semiconductors possessed sufficient known properties to make them by far the most interesting materials for wartime and, post-war, for commercial uses. As a consequence, almost all of the scientific investigations were centered on these materials. The compounds are more difficult to prepare, and consequently, it was not possible at that time to investigate their physical and electrical properties systematically. Because of differences in the bonding scheme of the atoms, the models developed for the covalently bonded materials (Si and Ge) could, in general, not be extended to other materials. However, it was known that some semiconducting compounds form wurtzite and zinc-blende lattice structures and, hence, that the binding mode of these materials is similar to that of germanium and silicon. Materials known to crystallize in the above forms include II-VI compounds such as zinc sulfide, I-VII compounds such as AgI, and III-V compounds such as AlN. In the early 1950's several investigators began to explore the properties of some of these materials. H. Welker was the first to make a thorough and systematic study of the III-V compounds (106-108). His investigations showed that these compounds were indeed semiconductors and that they had some very interesting properties, some of them very similar to those of silicon and germanium. The properties of some of the materials, such as indium antimonide had obvious technical possibilities, and interest in the III-V compounds was greatly increased as a result of this work. The publication of Welker's work was followed by a host of studies on the electrical and optical properties of III-V compounds. A good bibliography for this

work can be found in Madelung's book (109). Also around this period, interest in the semiconducting properties of the II-VI compounds (110, 111, 112) as well as of compounds from other elements began to rise. Smith (111), investigating conductivity, found that cadmium sulfide exhibited only n-type conductivity. Reynolds et al (112), while investigating conductivity and rectification in cadmium sulfide, observed photo-voltaic effects. The interest in the properties of these materials resulted in rapid advances in the technologies for their preparation, and by the middle 1950's the possibilities of devices fabricated from these materials began to be explored in earnest.

3. Junction Formation

a. *Early Techniques:* The earliest rectifiers were of the point-contact or cat-whisker type (90, p. 6). This type of device was adequate, albeit at times frustrating, for detector use in early radio and later microwave and radar work. Major disadvantages of this contact type included instability, unreliability, and limited power-handling capability. The introduction of alloyed junction techniques (113), whereby donor or acceptor type metal electrodes are fused to a homogeneous silicon or germanium crystal by heating (114, 115), resulted in diodes with a high degree of reproducibility, very low reverse currents, good temperature stability, improved high-frequency performance, and good power-handling capabilities (116). These techniques were readily applicable to devices of relatively small area and were good for fabricating general-purpose diodes and zener diodes. However, the alloying techniques proved difficult to apply to large areas, and were therefore not practical for the early development of necessarily large-area devices such as high-power rectifiers and solar cells.

The first broad-area p-n junctions to be made under controlled conditions were produced by the grown-junction technique of Teal, Sparks, and Buehler (117). Using the Czochralski crystal-pulling process, they introduced the necessary impurities during the growth of a germanium crystal to change the conductivity type. This produced a crystal with one portion having n-type conductivity and the other portion having p-type conductivity, with a p-n junction at the interface. These junctions were found to approach very closely the ideal conditions and were used in experiments to verify the quantitative features of Shockley's diode theory (118). However, silicon junctions produced by the same technique were not so well behaved, exhibiting anomalous reverse saturation current behavior (119). It was suggested that the large values of saturation current were caused by the generation of carriers in the space charge region (114). The alloyed- and grown-junction techniques were developed at about the same time.

b. *Diffused Junctions:* The "power-formed" or "welded" variety of point contacts used in early general-purpose diodes (1N34) were actually diffused junctions formed at relatively low temperatures and short diffusion times and were recognized as such by the researchers who made use of this technique. Alloyed junctions, which are actually solution-grown junctions based on the regrowth heat cycle after alloying, were used in some of the early attempts to study the diffusion of impurities in semiconductors (120, 121), a phenomenon which began to be investigated in the early 1950's. The object of these

studies was to measure and calculate the extent of the thin diffused region under the alloy. The more practical system (from a device and production point of view) of high-temperature vapor diffusion was not introduced until 1954. In 1954 Fuller and Ditzenberger (122, 123) reported the successful fabrication of p-n and n-p junctions by heating single-crystal silicon of n-type or p-type conductivity in the presence of boron trichloride or phosphorus vapor, respectively. The temperatures used ranged from 1050°C to 1250°C, with diffusion times between 16 and 112 hours. The process was immediately applied to the fabrication of power rectifiers (123) and of a p-n junction photovoltaic energy conversion device (124). Similar work on high-temperature diffusion was reported by Dunlap et al. (125) at approximately the same time. The introduction of this process caused not only more intensive studies of the diffusion process itself, but also a veritable epidemic of work on diffused junction transistors and other devices. A bibliography of this work can be found in the paper by F. M. Smits (126).

In summary, the materials preparation work of the 1940's and the development of the diffusion technique for the introduction of impurities and junction formation provided the foundation for today's semiconductor device technology. During this period, the purity of the materials produced was raised by at least three to four orders of magnitude (from a prewar best of about 10 ppm), and techniques for growing single crystals of semiconductors with dislocation densities of the order of 10^2 cm^{-2} or less (germanium) were developed. The refinement of these techniques to extend their capabilities and to permit precise control as well as the possibility of introducing predetermined impurity profiles over large areas were the final steps necessary for large-scale device production. In the course of these early developments on elemental semiconductors a new understanding of the properties was built up and previously unknown effects were discovered, among them the p-n junction photovoltaic effect.

C. EXPERIMENTAL SOLAR CELL DEVELOPMENT

In the years between 1940 and 1950, photovoltaically sensitive p-n junctions were discovered in a number of materials including silicon, germanium, and lead sulfide. Although the phenomenon was first discovered in silicon, most of the experimental investigations of the effect during this period as well as the early 1950's were performed on germanium samples. This was primarily due to the much more rapid advance of the germanium technology, which was caused by the greater chemical inertness of this material. The effect was not seriously considered for energy conversion purposes until the introduction of junction formation by diffusion in silicon which took place in the mid-1950's. It was also at this time that other materials, the compound semiconductors, came into consideration.

1. Selenium and Germanium Photovoltaic Cells

As was mentioned in Section II selenium photovoltaic cells appeared to be of little scientific interest after about 1930, although they continued to be used in photoelectric

detectors. It is of historical interest, however, to make a brief mention of some work published in the late 1940's. This work was concerned with the energy conversion efficiency of the selenium barrier layer photocell and appears to be the first instance in which a solid-state photovoltaic cell was considered as an energy conversion device.

In 1948, R.A. Houston, disturbed by claims of 50% conversion efficiency from light energy to electrical energy contained in a leaflet accompanying a commercial photocell, undertook a series of experiments which were intended to determine the actual efficiency of the cells (127). Houston found a maximum efficiency of 6.2×10^{-5} for white light illumination, while the efficiency for monochromatic light was 6.4×10^{-8} (at 636 μm). These experiments lacked in several aspects. These include the facts that the light level was extremely low for the monochromatic measurements and that the load resistance was far from optimum. Although other factors influencing these measurements, including the quality of the cells and the characteristics of the filter used, cannot be determined any more, however, it is safe to assume that the results were too low. However, this work is of interest because it constitutes the first (although admittedly crude) attempt to evaluate the energy conversion capabilities of a photovoltaic device and because it stimulated more careful study by some other investigators. Billig and Plessner (128), disturbed in their turn by the results of Houston, published, in the following year, their own studies on the efficiency of selenium barrier layer photocells. First, using the theoretical expressions of Lehovec (129) and manufacturers' data, they showed that an efficiency of 1 to 4% for monochromatic light near 550 μm should be expected. A typical photocell I-V characteristic (fourth quadrant) was shown in the referenced paper, with maximum power point indicated. The cells were apparently badly limited by series resistance as indicated by the quoted typical fill factor value of 0.36. Measurements were made on actual cells. Care was taken in optimizing the load resistance and isolating the wavelength of the radiation. An efficiency of 1.41% was measured for the mercury green line with an incident intensity of $0.73 \text{ mW}\cdot\text{cm}^{-2}$ while a sunlight measurement (January on a cloudy day, with no collimation) gave a maximum efficiency of 0.95%. These values agreed fairly well with the predicted values, and the authors concluded that Houston's results were in error. While these experiments were stimulated by academic rather than practical considerations, they were the first published experiments in which photovoltaic energy conversion was seriously investigated. Further consideration was not given to this subject until the introduction of the Bell solar battery.

Photovoltaic effects in germanium were first observed by P.R. Bell at the Radiation Laboratory of the Massachusetts Institute of Technology around 1944 (Reference 90, p. 393). These observations led to a detailed study by S. Benzer, whose results appeared in NDRC reports in November 1944 and October 1945 (ibid.), but were not published in the general literature at the time. The first published mention of photovoltaic effects in germanium appeared in 1946 in the form of abstracts of two talks given at American Physical Society meetings in April and June of that year (130, 131); in these abstracts the photosensitive properties of certain germanium crystals when contacted by metal points, were described. The crystals contained naturally occurring n- and p-type regions. Two types of behavior were observed and were labeled photodiode and photo-peak behavior, respectively. The photodiode behavior was that which one would expect when

operating a photocell at reverse bias. The photocurrent was found to vary linearly with intensity at a rate of several milliamperes per lumen for white light and to be independent of voltage. The threshold wavelength for stimulating photovoltaic response was observed to be approximately $1.5 \mu\text{m}$ with peak response occurring at about $1.3 \mu\text{m}$. The photo-peak behavior is somewhat more unusual, and the abstract does not provide sufficient information to deduce the nature of the effect. The devices which exhibited this effect had I-V characteristics similar to that shown in Figure 8. The voltage peak, which occurred before the negative resistance region in the I-V characteristic was reached, was reduced by illuminating the devices, and at high illumination levels the peak (and hence the negative resistance region) was eliminated. Heating was observed to have a similar effect on the peak. The effect could possibly be explained as being due to two opposed diodes, one of which undergoes zener breakdown. This structure agrees with that indicated by Benzer in later publications.

In 1947, Benzer responded to remarks by L. Sosnowski who speculated that p-n junction photosensitivity, similar to that which he had observed in lead sulfide (132), might also be observed in silicon and germanium. Benzer stated (133) that such effects had indeed been observed and investigated in germanium. He described, briefly, some of the results of the earlier work under the NDRC. The structure that was investigated in this work is shown in Figure 9. The inhomogeneity of the crystal (n- and p-type regions)

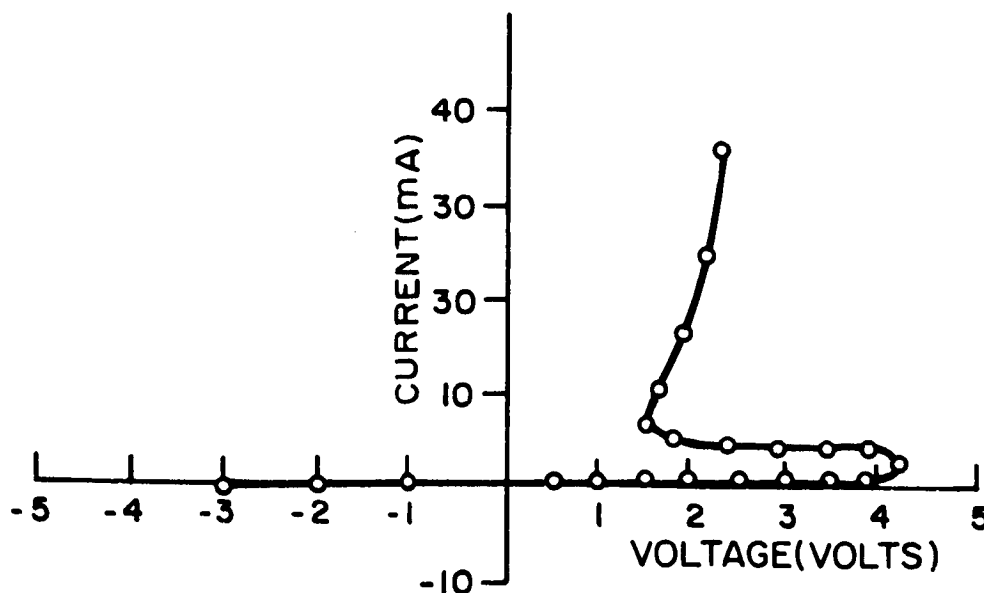


Figure 8. "Photoppeak" characteristic

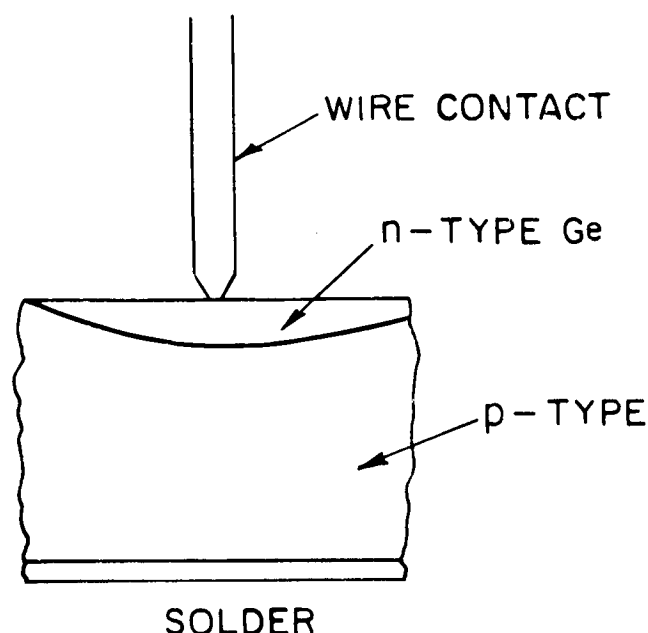


Figure 9. Photodiode structure, after S. Benzer

was apparently not intentionally produced. The device had a peculiar I-V characteristic (Figure 10) which was apparently due to the presence of two barriers, one at the metal-semiconductor contact and the other at the p-n junction. Both photovoltaic and "photoconductive" effects were noted as well as negative resistance and "self-oscillations". The "photoconductive" effects appear, in actuality, to have been photodiode type behavior (i. e. , the I-V characteristics shift but do not rotate). Magnitudes of the photovoltages observed are not given.

Three years after Benzer's letter was published, Becker and Fan (134) published data from experiments on germanium p-n junctions in which it was verified that the photovoltage varies linearly with light intensity for low intensities and more slowly for high intensities as predicted by Fan in a previous publication (135). Data on the temperature dependence of the spectral response of the photovoltage and the variation of photovoltage with load resistance were also given in this paper. Other investigations were reported by F.S. Goucher et al. (118) and by W.J. Pietenpol (136) both of whom used p-n junctions prepared by the grown-junction technique described in Section III-B-3-a above. Most of the device-oriented interest in the p-n junction photoeffect during this period was centered on its possible use in low-intensity radiation detection, as illustrated by the papers of Rothlein (137, 138) and Shive (139). These studies were concerned primarily with the sensitivity of the photocurrent or photovoltage to changes in light intensity rather than energy conversion as such although Rothlein estimated the ratio of the energy developed by the cell to the incident energy to be of the order of 0.01 (for

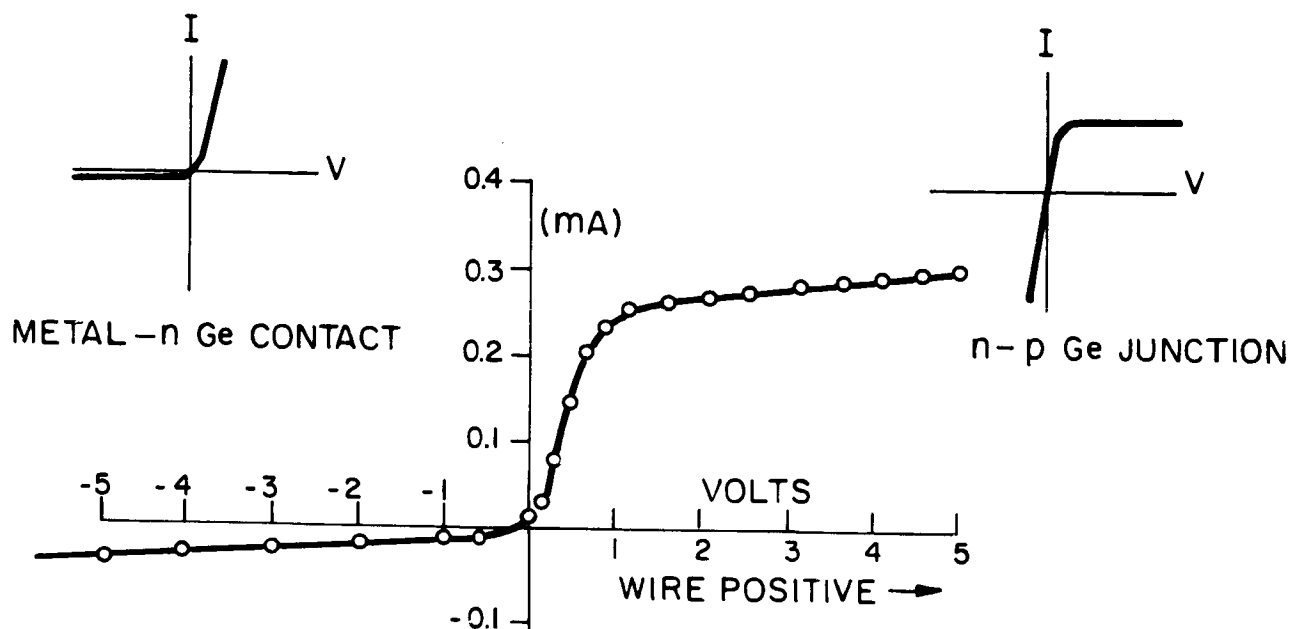


Figure 10. Current-voltage characteristic of photodiode

radiation corresponding to peak response). A brief interest in the energy conversion capabilities of germanium p-n junctions was roused when the results of Chapin et al. (124) on silicon were made public in 1954. Ruth and Moyer (140) published a letter in that year describing an experimental investigation of the variation of conversion efficiency with light intensity. Efficiencies up to about 0.5% were measured for intensities approaching that of sunlight (using a 3200°K photoflood lamp as a light source). The elimination of reflection losses and other improvements were expected to raise the efficiency to approximately 2%. Another investigation was published by Pfann and van Roosbroeck at about the same time (141). They considered the possibility of using p-n junctions as both radioactive (electron-voltaic) and photovoltaic power sources, and presented theoretical and experimental results both for silicon and germanium. From theoretical considerations the authors predicted an ideal efficiency of 18% for silicon solar cells under sunlight illumination. However, their experimental work dealt only with the electron-voltaic effect. As a result of this and other work (152) it became apparent that germanium was not ideally suited for solar energy conversion use. Consequently, the interest shifted to other materials which held more promise for this purpose, and very little further work was done with germanium photovoltaic cells.

2. Silicon Cells

Early in 1941, R. S. Ohl, a metallurgist at the Bell Laboratories, discovered in a melt of commercial "high-purity" silicon, a "well-defined barrier having a high degree of photovoltaic response" (87, 88). This observation marks the discovery of the p-n junction photovoltaic effect. The reasons for the occurrence of this junction were outlined in Section III-B-3 of this report, dealing with materials technology. Figure 11 is a drawing of the silicon melt showing the position of the naturally occurring photovoltaic barrier and a "surface type" photocell made from the barrier. In addition to the "surface type" cells, many of the cells were cut in the form of long rods or bars with the junction in the center normal to the surface. Figure 12(a) shows such a cell with a typical spectral response curve as shown by Kingsbury and Ohl (89). Figure 12(b) illustrates the variation of open-circuit voltage and short-circuit current with intensity for the "bar type" of cell. The "surface type" cells showed more response in the visible than the "bar type". The illumination source for the intensity dependence measurements was a 2848°K tungsten lamp. The cells were noted to be extremely stable under drastic temperature changes. Heating to red heat and immediately quenching in water apparently had no effect on the cell characteristics. Some of the cells were used in test circuits for ten years without any serious change in their properties. Ohl took the precaution of immediately patenting the device, but, it appears, did not publish his findings in the general literature or in an NDRC report until 11 years later. J. H. Scaff, who had worked with Ohl and also held a patent on the device, mentioned some of the findings in a paper published in 1949 (88). It is apparent, however, that Ohl's findings were not generally known, since Torrey and Whitmer attributed the discovery of photovoltaic effects in silicon to Miller and Greenblatt (Ref. 90, pages 392 and 393) around 1944 to 1945. Miller and Greenblatt's observations were made on point-contact rectifiers, and it is not clear if p-n junctions were present. Currents of $0.15 \mu\text{A}$ were obtained under illumination intensities of $12 \text{ mW} \cdot \text{cm}^{-2}$ of monochromatic light (wavelength $1.5 \mu\text{m}$ - maximum of the spectral distribution curve). The magnitude of the photovoltage was not given. There was very little interest in the photovoltaic properties of silicon during the

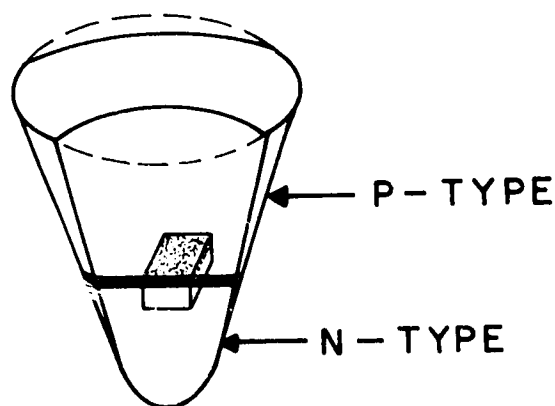


Figure 11. Representation of melt, showing photovoltaic barrier and photocell, after Ohl

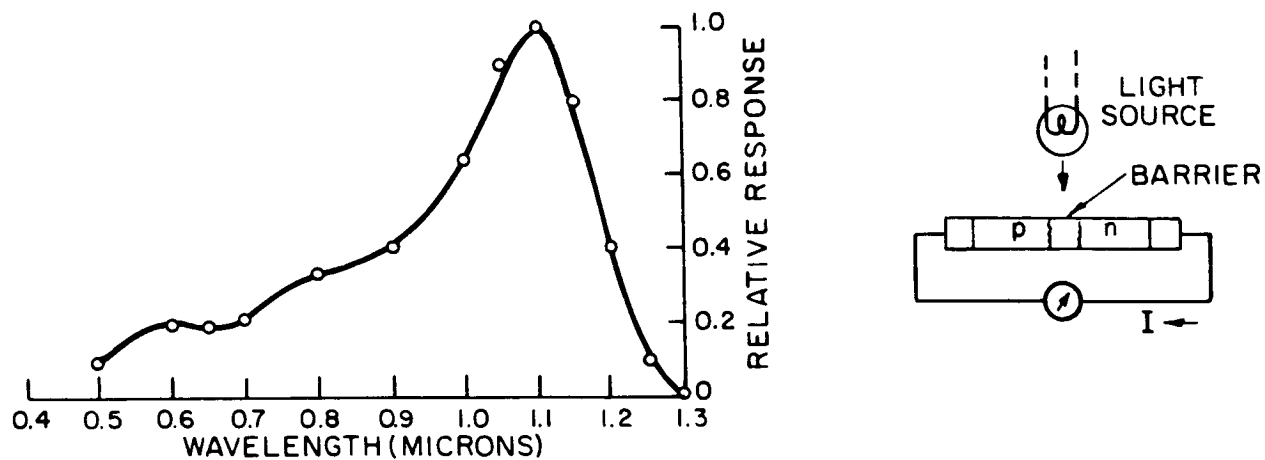


Figure 12(a). Spectral response (equal energy) of silicon photocell, after Ohl

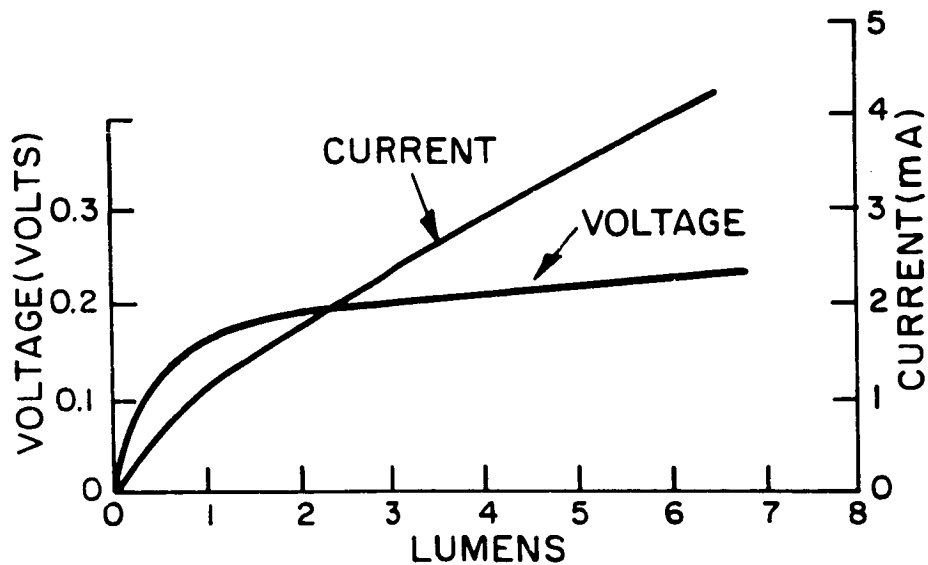


Figure 12(b). Illumination dependence of photocell current and voltage, after Ohl

period between the early 1940's and the early 1950's. Some observations on contact potential changes under the influence of light were published by Brattain (142) but these were concerned with surface state studies.

The next publication of interest was that of Kingsbury and Ohl (89) in 1952. After a brief account of Ohl's earlier work the authors discussed some experiments on the formation of photovoltaically sensitive barriers by ionic bombardment of silicon. This work was motivated by a search for techniques whereby large areas of silicon surfaces might be uniformly activated (i.e., a barrier formed). Such a technique was expected to produce photocells competitive with those available at the time. "Hyper-purity" silicon was used in this work to avoid the formation of natural barriers by impurity segregation. The activation process consisted of exposing the polished face of a silicon wafer to a uniform beam of helium ions with energies ranging from 100 eV to 30 keV. The pressure during bombardment was 10^{-3} to 10^{-4} mm Hg, and the silicon surface was maintained at a temperature of 395°C. Three cell sizes were constructed, with areas of 0.005 cm², 0.40 cm², and 8.0 cm². Most of the measurements were made on the intermediate area cells. The wafer thickness was 0.025 in. Attempts were made to evaluate the relation between ion velocity and junction depth by measuring spectral response as a function of accelerating voltage. Cells subjected to extremely low energy bombardment (100 to 226 eV) showed a definite blue shift (sensitive at shorter wavelengths), but bombardment at intervals in the higher energy range (570 eV to 30 KeV) yielded cells which, while more red sensitive than the low energy cells, were essentially identical among themselves. Figure 13 shows the spectral response curves of a blue shifted and a "normal" cell. In addition, cells made with relatively impure silicon were found to be blue-shifted compared with those made with pure silicon. To obtain highly photosensitive cells it was necessary to maintain the silicon at an elevated temperature during bombardment. The optimum temperature was found to be around 395°C. Cells made at temperatures above this had soft reverse characteristics while those made at lower temperatures had poor photosensitivity. The ion-bombarded cells were extremely stable and had photosensitivities of the order of 3000 μ A per lumen for tungsten light and for daylight. Although Kingsbury and Ohl were interested in developing competitive photodetectors rather than an energy conversion device, this work was the precursor of the more recent investigations of ion-bombardment techniques for solar cell fabrication.

The development of high-temperature vapor diffusion techniques by C.S. Fuller around 1953 to 1954 solved the problem of "uniformly activating" large-area semiconductor surfaces. This made it possible for Bell Laboratories to demonstrate their solar battery in April 1954 at the annual meeting of the National Academy of Sciences in Washington (143). The device was developed by G.L. Pearson, C.S. Fuller, and D.M. Chapin, (Physicist, Chemist, and Electrical Engineer, respectively). At about the same time the developers published data on the characteristics of the device (124). The cells had an open-circuit voltage of approximately 0.5 V and a conversion efficiency of 6% under sunlight illumination. The diffused layer thickness was 0.0001 in. A theoretical computation indicated an efficiency limit near 22% for the device. The actual device was limited by several practical factors which were thought to include reflection losses

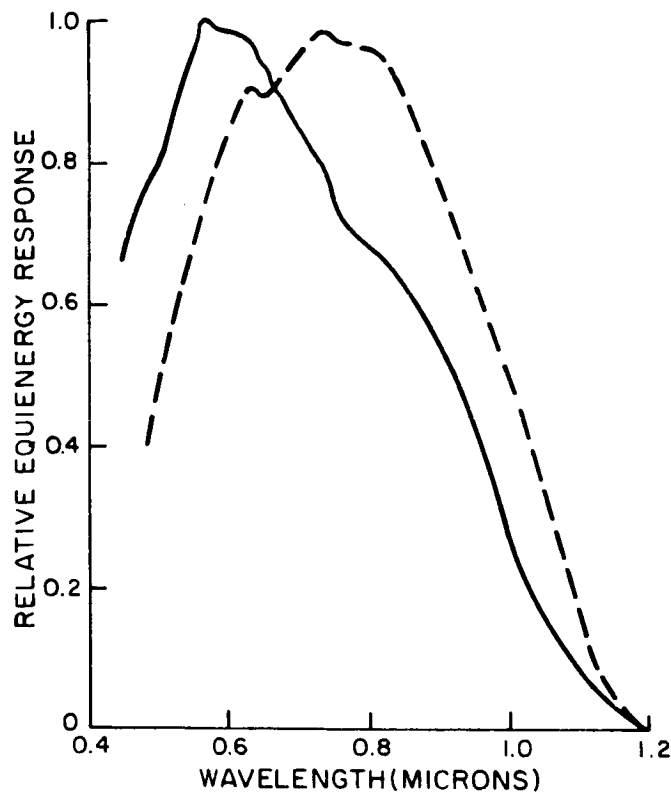


Figure 13. Blue shifted and "normal" ion-bombarded photocell responses, after Kingsbury and Ohl

approaching 50% and large series resistance losses, primarily in the thin p-type diffused region. Improved surface treatments were expected to improve the reflection problem while special contact geometries were planned to deal with the resistance of the diffused layer.

A number of publications followed the initial work, including a second one by Chapin, Fuller, and Pearson, providing more detailed information, presented in a popularized fashion (144). Figures 14(a) and 14(b) contain a cutaway view of the "Bell Solar Battery" and a plot of the intensity dependence of the device characteristics respectively. The open-circuit voltage for sunlight illumination is seen to have been approximately 0.52 V and the short-circuit current density was $25 \text{ mA} \cdot \text{cm}^{-2}$. The cell was considered for use as a power source for telephone amplifiers in remote areas, and results on battery-charging studies under varying weather conditions were presented. This publication appeared one year after the initial disclosure, and mentioned that at this time the average efficiency had been raised to 8%, with some units reaching 11%. In the same year (1955), Prince published a paper (145) which compared theoretical predictions with experimental results on silicon cells. The results of this study indicated that the most serious problem limiting the efficiency of the early devices had been series resistance in the contacts. The theory showed that total series resistance could and should be reduced to less than 1 ohm, partially through adoption of suitable cell geometry. Prince also investigated the use of antireflection coatings to reduce reflection losses. An experiment which attempted to use a piece of soft glass cemented to the cell surface did not improve the short-circuit

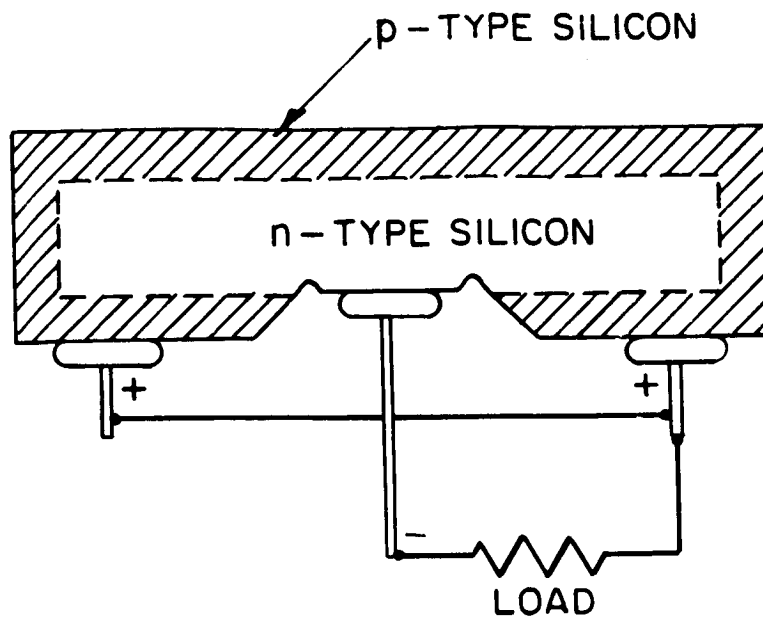


Figure 14(a). Cross section of Bell solar battery, after Chapin et al.

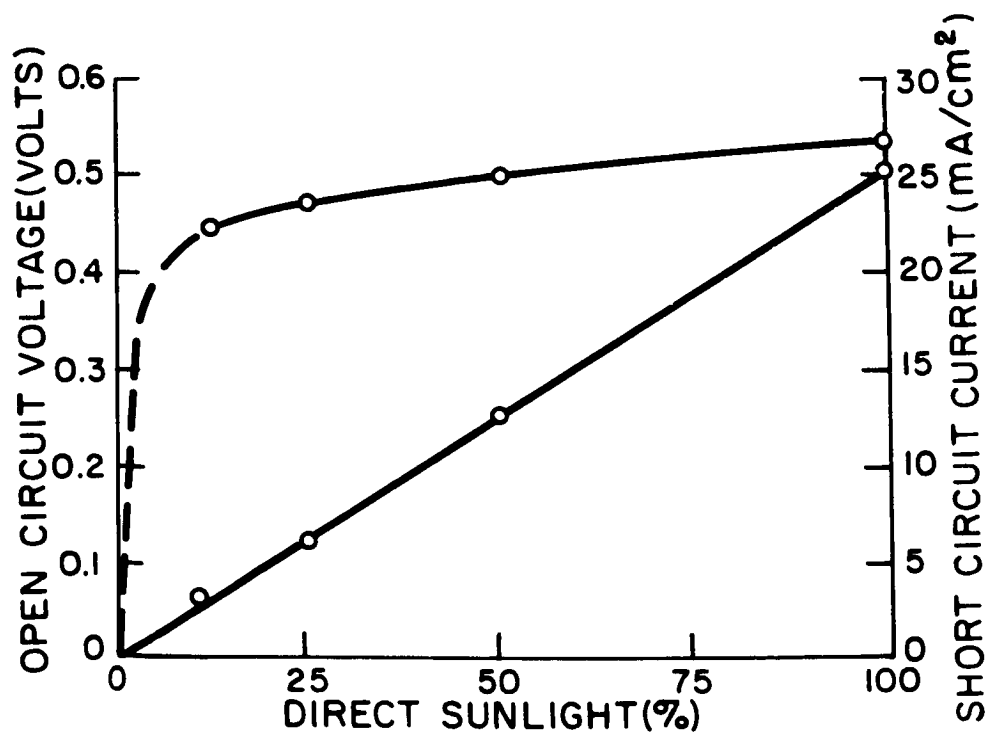


Figure 14(b). Intensity variation of Bell solar battery characteristics

current. The results of the experiment were explained as possibly due to a silicon dioxide layer on the cells, which would provide antireflection properties.

From this beginning silicon has continued to dominate the field of photovoltaic energy conversion to this day. The success of silicon, however, did stimulate interest and work on other materials. These developments are discussed in the following section.

3. Compound Semiconductor Photovoltaic Cells

Although most of the important developments in compound semiconductor solar cells occurred after the introduction of the Bell solar battery, the first reported observation of an identifiable p-n junction photovoltaic effect in a compound material was that of Sosnowski, Starkiewicz, and Simpson in lead sulfide in 1947 (132, 146). Photovoltaic effects had been observed in many compound materials, notably silver sulfide, several decades prior to the discoveries of Sosnowski, et al.; however, most of these observations were associated with contact phenomena and were not identifiable as p-n junction effects. In a paper authored by Starkiewicz, Sosnowski, and Simpson (147) in 1946, photovoltaic effects in lead sulfide films under infrared illumination ($1\text{ }\mu\text{m}$ to $3.5\text{ }\mu\text{m}$) were reported. The effect observed was actually a "high-voltage photovoltaic effect", since the measured photovoltage (2V) was greater than the bandgap. Sosnowski et al. (146) postulated a multi-p-n junction mechanism to explain the effect and constructed such junctions experimentally by bringing together two pieces of lead sulfide, one containing excess lead and the other containing excess oxygen. The junctions were extremely thin and their operation was thought to be governed by "diode theory" rather than diffusion theory. Sosnowski reported that he observed photovoltaic effects across such junctions and developed a theory to explain his observations. Unfortunately, he gave no indication as to the magnitude of the photoeffects observed. Because of its narrow bandgap (0.3eV), lead sulfide is not of interest for photovoltaic solar energy conversion applications, although it is an important material in infrared radiation detection. A number of other compounds with energy bandgaps above 1 eV, are of interest, at least from a theoretical point of view. The most important of these fall into the groups of II-VI and III-V compounds. The developments on these are discussed in the remainder of this section.

After the establishment of the semiconducting nature of the III-V compounds by Welker (136), these materials attracted considerable attention among investigators interested in new photoconductors. Many of the experiments led to the discovery of photovoltaic effects in these materials. Talley and Enright (148) reported having observed photovoltaic effects in indium arsenide. The photovoltages were detected across p-n junctions which occurred naturally in grown ingots of the material, and which were located by thermoelectric measurements. Figure 15 is a graph of the photoresponse of a typical indium arsenide photovoltaic cell as measured by Talley and Enright. The measurements were made at liquid-nitrogen temperature. Photovoltaic effects were observed at room temperature but increased by three order of magnitude at the lower temperature. The response of the cell was primarily in the infrared with a bandgap of approximately 0.27 eV, making it of little interest in solar energy conversion.

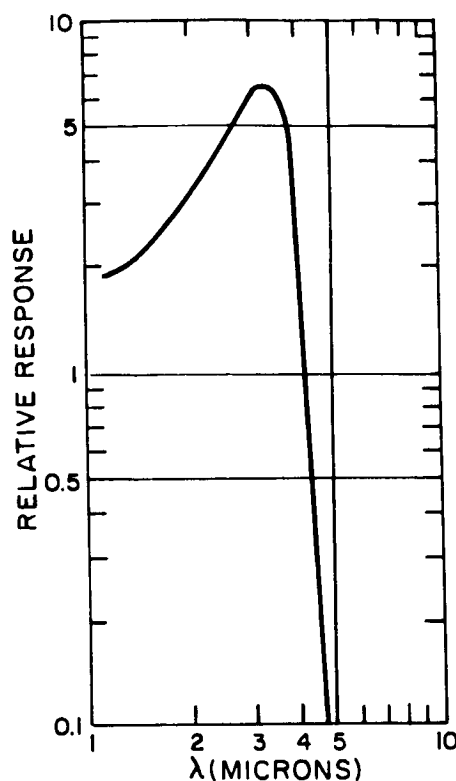


Figure 15. Photoresponse of an InAs photovoltaic cell at 77° K, after Talley and Enright

There were two reported observations of photovoltaic effects in indium antimonide in 1954. The first was that of D.G. Avery et al. (149) who were studying photoconductive effects. The second was by G.R. Mitchell et al. (150) who had intentionally produced photovoltaic cells by the grown-junction technique. The observations of Avery et al. were made on a point-contact device consisting of a piece of pure single-crystal indium antimonide contacted by a tungsten probe. Spectral sensitivity measurements were made at about room temperature. The data showed the sensitivity beginning to rise at a wavelength of about 8 μm reaching about 80% of peak at 7 μm (0.176eV). For wavelengths shorter than 6 μm the photodiode exhibited an approximately constant energy sensitivity (i.e., response per unit energy input). The measurements of Mitchell et al. were made at 77° K and indicated a band edge corresponding to 5.7 μm (0.22eV) at this temperature. Most of the discussions in this paper were concerned with the signal-to-noise ratio of the photocell. Again the material is not of interest for solar energy conversion.

Welker himself seems to be the first to report photovoltaic effects in gallium arsenide. In a survey paper on "Semiconducting Intermetallic Compounds" published in 1954, he showed the I-V characteristics of a GaAs photocell under several intensities but gave no discussion (107). Figure 16 shows these characteristics. In the following year Gremmelmaier reported his findings (151) on a photocell with an area of 23 mm^2 which was cut from polycrystalline material. The n-type crystal had a layer of p-type

material about 10^{-2} mm thick grown onto its surface. Under sunlight illumination (sea level) the cell had an open-circuit voltage of 0.66 V, a short-circuit current density of $2.6 \text{ mA}\cdot\text{cm}^{-2}$ and an efficiency of about 1%. Under focused sunlight an open-circuit voltage of 0.87 V and a current density of $70 \text{ mA}\cdot\text{cm}^{-2}$ were obtained. Figures 17(a) and 17(b) show the intensity variation of the photocurrent and photovoltage. The photovoltage was surprisingly linear with intensity at intensities approaching that of sunlight. The details of the measurements were not given. A second photocell was made and had an efficiency of approximately 4% under a sunlight intensity of $60 \text{ mW}\cdot\text{cm}^{-2}$. This cell had an open-circuit voltage of 0.73 V and a current density of $4.8 \text{ mA}\cdot\text{cm}^{-2}$. Gremmelmaier anticipated considerably higher efficiencies from single-crystal cells.

In 1955, working under an Army Signal Corps contract, Loferski, Rappaport, and Linder of RCA developed a theoretical analysis which indicated that a number of the III-V compounds (InP, GaAs, and AlSb) as well as at least one of the II-VI compounds (CdTe) should yield photovoltaic cells with efficiencies higher than silicon (152). Later that year Jenny, Loferski, and Rappaport (153) reported measurements on cells made by diffusing cadmium into n-type gallium arsenide wafers in which efficiencies as high as 6.5% were achieved. The analysis of Loferski et al. (152) indicated that gallium arsenide was the most promising of the III-V compounds from a combined theoretical and technological point of view, and as a result, a large percentage of the effort to develop alternative solar cell materials has been expended on gallium arsenide.

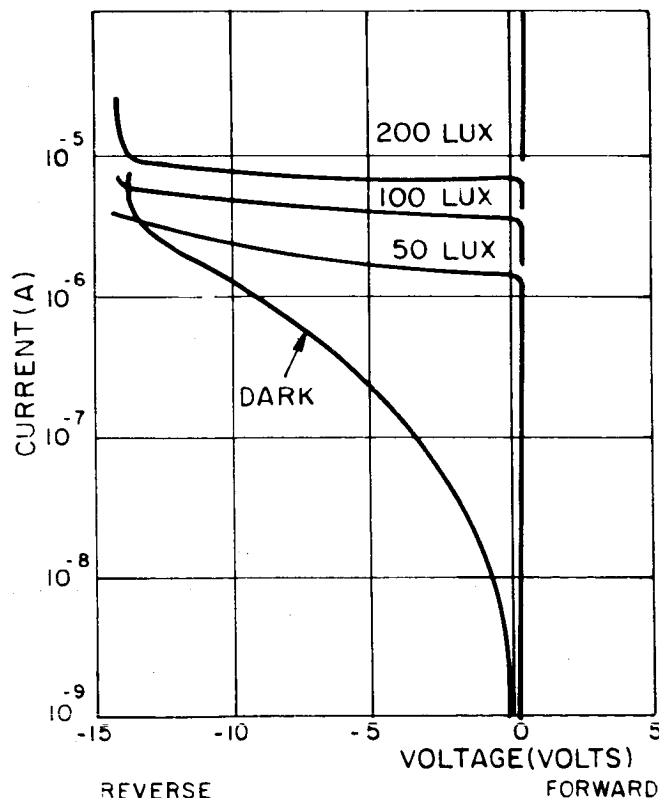


Figure 16. Current-voltage characteristic of GaAs photocell for different intensities, after Welker

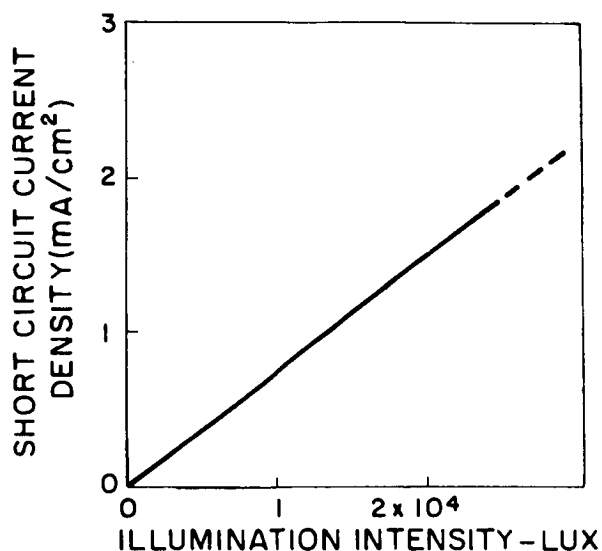


Figure 17(a). Variation of open-circuit voltage with intensity for GaAs photocell, after Gremmelmaier

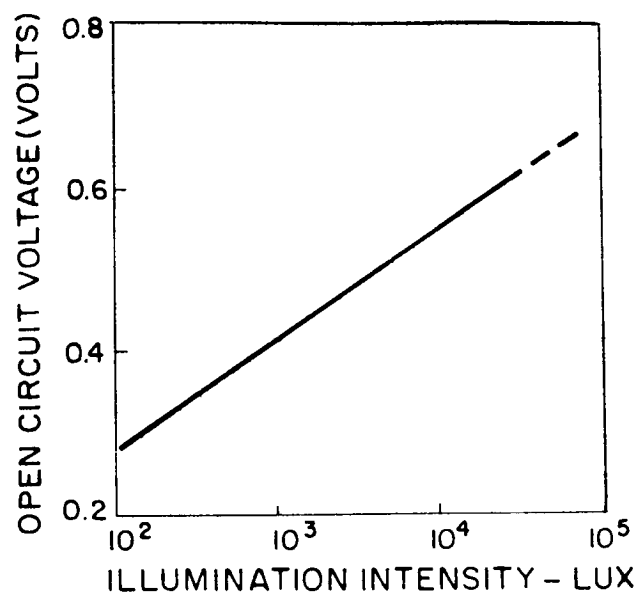


Figure 17(b). Variation of short-circuit current with intensity for GaAs photocell, after Gremmelmaier

Of the II-VI compounds which aroused the interest of investigators during the early and middle 1950's, cadmium sulfide and cadmium telluride were the most outstanding and the only two on which any significant amount of work toward photovoltaic solar energy conversion was done. Cadmium telluride derived interest from the fact that its bandgap is near the optimum for solar energy conversion as indicated by the analysis of Loferski et al. (152). The investigations of cadmium sulfide, which started earlier and became more extensive, however, arose from a completely different set of circumstances. Cadmium sulfide's bandgap (2.4eV) is so large, that, at normal temperatures, it should be relatively inefficient for photovoltaic solar energy conversion since a considerable portion of the sun's photons are not energetic enough to excite carriers in the intrinsic material. D.C. Reynolds and G.M. Leies, in the course of investigating photoconduction and rectification in cadmium sulfide, discovered pronounced photovoltaic effects (154).

The first observations of the photovoltaic effect in cadmium sulfide occurred while testing cadmium sulfide rectifiers. The rectifiers were constructed by attaching an indium base electrode and a top electrode of silver, copper, gold, or platinum to crystals approximately 3 mm thick. The electrodes were apparently opaque but when the rectifiers were illuminated from the side, some of them were found to be photovoltaically sensitive. Open-circuit voltages of 0.4 V, and short-circuit current densities as high as 15 mA·cm⁻² were observed under sunlight illumination. The spectral response of these photovoltaic effects did not conform to that predicted on the

basis of the bandgap of cadmium sulfide (155), but showed a considerable peak in the red, which in some crystals was higher than that of the intrinsic (green) peak (Figure 18). It was also observed that the short-circuit current at a given wavelength was dependent on the wavelength of light used in prior illumination of the crystal. These effects were attributed to the presence of an impurity band in the forbidden zone into which a portion of the excited electrons could pass. If these electrons were long lived and could move freely in the impurity band, then it would act like a conduction band, assuming the proper electrode conditions. This was felt by Reynolds to be the most plausible mechanism to explain both the photoconductive and photovoltaic effects observed (156).

Photovoltaic effects were also observed in compressed cadmium sulfide powders, although the photocurrents were relatively low. The discovery of the unusual photovoltaic properties of cadmium sulfide when treated with certain metals initiated a series of investigations into the energy conversion possibilities of this material, especially in thin-film form, which is still in progress. Many of the peculiar properties discovered in the earliest cadmium sulfide photovoltaic cells are still eluding a satisfactory explanation by today's investigators.

The photovoltaic properties of cadmium telluride received very little experimental attention until after 1955. The fact that photovoltaic effects had been observed in cadmium telluride was mentioned in one of the early Signal Corps reports written by RCA Laboratories investigators (152), but no details were given. As mentioned, theoretical analysis showed that cadmium telluride should have an efficiency exceeding that of silicon on the basis of the width of its bandgap. As a result, cadmium telluride was subjected to intensive developmental work during the years following 1955.

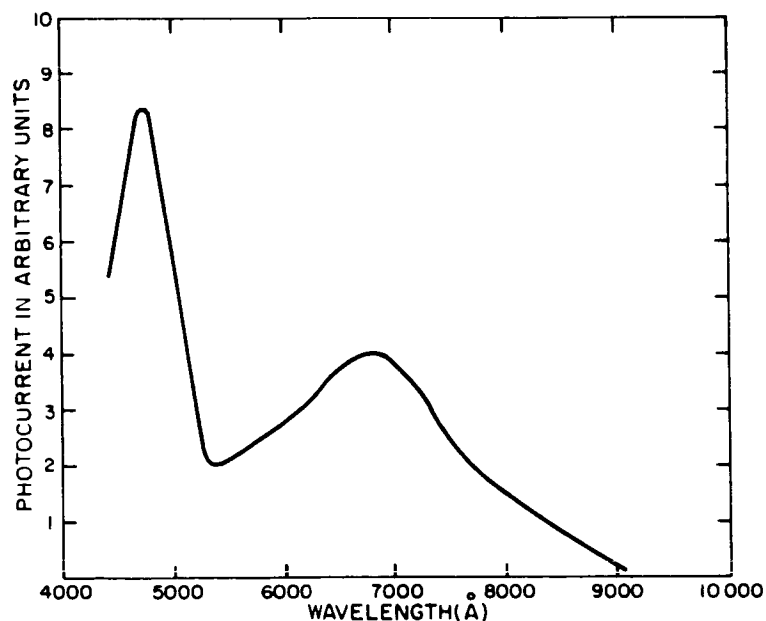


Figure 18. Spectral response of a CdS crystal with silver and indium electrodes, after Reynolds

D. DEVELOPMENT OF THE THEORY

1. Progress in Supporting Fields

The development of a satisfactory theoretical account of semiconductor rectification by Mott and Schottky during the late 1930's was based in part on supporting work in solid-state theory during the same period. It would be inappropriate to trace this in detail here, but some mention of the main points is in order.

The most important development was the band theory of energy levels in solids. This was derived from the quantum theory, originally by M. J. O. Strutt in 1928, with mathematical investigation of the concept by L. Brillouin, P. M. Morse, R. Peierls, and R. L. Kronig and W. G. Penney in 1930 and 1931. Seitz's book (157) on solid-state theory, originally published in 1940, reviews the development of the subject, and gives a full account of the state of the theory up to the late 1930's. The explanation given by this theory of the differences in electrical behavior of metals, semiconductors, and insulators is, of course, that used at the present time. For pure semiconductors, the electrical properties were shown to be determined by that part of the electronic band structure which consists of a lower-energy band (valence band) whose states would be completely filled by electrons at zero absolute temperature, separated by an energy gap, from a higher-energy band of allowed states (conduction band) which would be unoccupied at 0°K. The situation is as illustrated in Figure 19(a). The energy gap between the two bands represents a range of energies which the electrons cannot possess ('forbidden bandgap'), because of the restrictions described by the quantum theory. This remains true in a chemically pure single crystal of a semiconductor even when the temperature is raised above absolute zero. However, as the temperature is raised, there exists a finite increasing probability that a few electrons may acquire sufficient thermal energy to transfer from the lower (valence) band into the upper (conduction) band.

Since electrical conductivity requires that motion in a preferred direction be imparted to electrons by an electric field, some electrons in a solid through which a current is passing must have higher energies than electrons in a solid not carrying a current. In a semiconductor at absolute zero, the electrical conductivity must therefore be zero since there are no allowed higher energy states available to electrons, all energy levels in the valence band being occupied, unless they can cross the forbidden band. Normal electrical fields cannot supply sufficient energy to an electron to permit it to make the transition across the bandgap. However, if the temperature is raised above absolute zero, thermal excitation can provide sufficient energy to permit some electrons to occupy states in the higher energy band. Now each band consists of allowed energy levels separated by extremely small energy increments. Hence, application of an electrical field at a temperature other than absolute zero causes electrons in both bands to move by transferring to allowed states of very slightly higher energy. These are available both in the higher-energy band (because its states are normally unfilled), and in the lower-energy band, because electrons can transfer into states left vacant by electrons thermally excited into the higher band. It was realized that the latter process could be regarded as the motion of a charge of equal magnitude and opposite sign to that of an electron, and this concept of 'hole' conduction was used immediately by Mott and others.

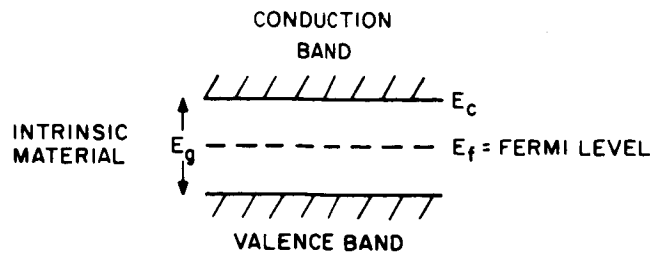


Figure 19(a). Band structure for intrinsic semiconductor.

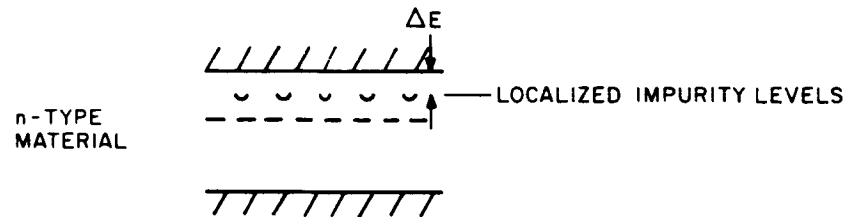


Figure 19(b). Band structure for n-type semiconductor.

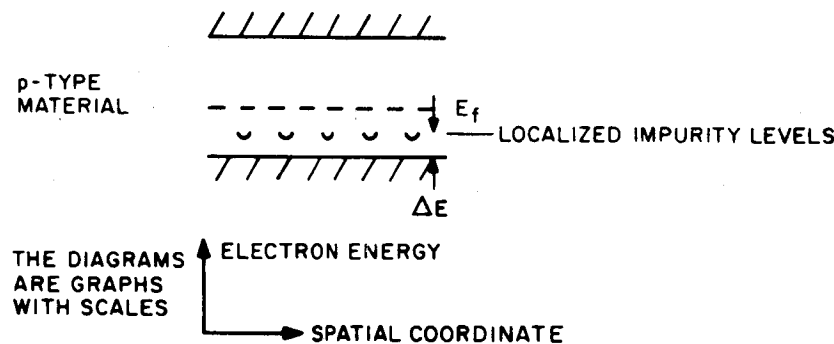


Figure 19(c). Band structure for p-type semiconductor.

Now the experimental work of Schottky had shown that small amounts of chemical impurities or departures from stoichiometry could cause the conduction process to be greatly enhanced, and to be dominated by either motion of electrons in the conduction band or by motion of holes in the valence band.

The theory showed that these effects could be explained by the creation of allowed energy states within the forbidden bandgap, these states lying close to one of the semiconductor band edges, and being spatially associated with the impurity atom giving rise to the energy level. If the species causing the state also provided an electron to fill the state at absolute zero, then at a higher temperature the electron could transfer to the conduction band. Species having such properties are called donors. The probability of transfers to the conduction band occurring is much enhanced for electrons occupying energy states close to the conduction band. Based on such a large transition probability, only a small concentration of donors would be necessary to dominate the conduction process at relatively low temperatures, where the thermal transfer of electrons directly from the valence to the conduction band is unlikely. The converse process, leading to the

formation of holes in the valence band, occurs through the presence of a species providing an energy level close to the valence band, but no electron to fill it. Such species is called an acceptor.

It was found convenient to consider an energy level at which there would be a 50% probability for the occupancy of a state at that energy. This level is called the Fermi level (E_f), and for most cases of a semiconductor it lies inside the forbidden band. Then the probability $P(E)$ of occupancy of an energy level E by an electron is described by

$$P(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \quad (15)$$

Equation (15) is the Fermi-Dirac distribution function, often called "Fermi function", and is used frequently as a factor to a distribution of allowed energy states, thus describing their actual occupancy. In the general case, E_f does not have to represent an energy level half-filled with electrons, since E_f may be in the forbidden bandgap; then the Fermi level is a conceptual level only. The Fermi function, Eq. (15), characterizes a distribution such that there is an equal number of higher energy levels above E_f occupied, as there are unoccupied levels of energy less than E_f .⁵ The band-structure for three types of semiconductor can now be visualized, as shown in Figure 19.

In the early 1930's, both A. H. Wilson and R. H. Fowler provided methods for calculating the density of conduction electrons or holes. The results showed that

$$n = \frac{\nu}{2} \exp\left(\frac{-\Delta E}{kT}\right) \left[\left(1 + \frac{4N}{\nu} \exp\left(\frac{\Delta E}{kT}\right) \right)^{1/2} - 1 \right] \quad (16)$$

where

$$\nu = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \quad (17)$$

- n = density of electrons or holes
- m^* = effective mass of electrons or holes in the lattice
- k = Boltzmann's constant
- T = absolute temperature
- h = Planck's constant
- ΔE = energy difference between impurity level and adjacent band edge, as illustrated in Figure (19) for electrons or holes
- N = density of donors or acceptors

⁵It should be noted that at energies sufficiently removed from E_f (that is, $\frac{E - E_f}{kT} \gg 1$),

Eq. (15) describes the distribution obtained earlier by the methods of Maxwell and Boltzmann.

Thus, the electrical conductivity will increase exponentially with temperature until all the carrier-contributing species are ionized. Then the density of free carriers will remain constant with increase of temperature until sufficiently high temperatures are reached to allow thermal excitation across the bandgap to contribute a significant number of carriers. At still higher temperatures, the carrier concentration will then again increase exponentially with temperature, as in a pure semiconductor without impurity level.

This band theory was used by Mott and Schottky in their theoretical models accounting for semiconductor-metal junction I-V characteristics in 1939.

2. Continuation of Work on Rectification Theory

a. *Metal-Semiconductor Contacts (1940-46)*: The great deal of experimental work done on mixer and detector diodes for radar microwave systems during the second World War⁶, was accompanied by theoretical work by various groups. Notable among these were Bethe at the Radiation Laboratory of MIT, Seitz and others at the University of Pennsylvania, and Sachs and others at Purdue University.

The principal objective of this work lay in explaining the electrical behavior of point-contact metal-to-semiconductor rectifiers. The semiconductors used were silicon and germanium. In general, the I-V characteristics followed the expected exponential law, and the main consideration was to provide a theoretical explanation of the I_0 values in the diode equation, by analyzing the device models with various band structures. Because of the nature of the devices (a metal point pressed against the surface of a crystal of semiconductor), this amounted to finding the band structure at the free surface of a semiconductor. Bethe (158) analyzed this by integrating Poisson's equation with suitable boundary conditions, and concluded that at the metal-semiconductor contact a barrier region of 10^{-6} cm thickness would be formed. This analysis was done for silicon, and it was pointed out that a much thinner region would result if the semiconductor dielectric constant were to be considerably less than the value 13.0 of silicon. Bethe also noted that tunnelling and image forces which were considered in some earlier rectifier theories, do not contribute significant effects in this type of device, chiefly due to the large value of the dielectric constant possessed by silicon, and also germanium.

⁶A note on the literature of this period: Work during World War II was classified at the time and, hence, did not immediately appear in the open literature. The results were recorded in a series of contract reports, which were not declassified until 1960. A group of papers by some of those who had been involved in the work were presented at the Meeting of the American Physical Society at Cambridge, Mass., April 25-27th 1946. Abstracts for these papers are to be found in Phys. Rev. 69, 628 (1946). An account of the work was published in Vol. 15 of the Radiation Lab. Series (Reference 90) in 1948, from which most of the information in this section has been obtained, this being the most coherent source readily available.

Now this barrier thickness is much less than the 10^{-5} to 10^{-4} values measured in the copper-copper oxide rectifiers to which Mott's and Schottky's analyses applied. In fact, the barrier thickness in the silicon devices was now of the same order of magnitude as the mean free path of the carriers, and hence a diffusion analysis of the electrical characteristics was not applicable. Bethe discussed an alternative "diode analysis" which is applicable when scattering processes in the transit of carriers across the barrier can be neglected. This analysis is the same as that for the thermionic diode (hence the appellation), and is based on an electron distribution given by the Maxwell-Boltzmann approximation. Hence, the I-V equation is again of the same form as Eq. (12), but with a different J_0 value:

$$J_0 = nq \sqrt{\frac{2kT}{\pi m^*}} \exp \left(\frac{-q V_0}{kT} \right) \quad (18)$$

$$I_0 = (\text{device area}) \times J_0 \quad (19)$$

where V_0 = barrier height, as shown in Figure 7(a). When the barrier width is of the same order of magnitude as the mean free path, it is not immediately apparent that scattering processes can be neglected. However, Bethe pointed out that the mean free path should not be compared with the total boundary region thickness, but rather with the distance over which the potential changes by an amount kT .

In summation, Bethe analyzed the point-contact rectifier, showing that the electrical behavior could be reasonably well explained by the (thermionic) diode theory, with a boundary layer about 10^{-6} cm thick arising from the bulk properties of the semiconductor alone without the necessity for introduction of an electrically active species at the semiconductor surface to explain the barrier layer properties.

The results of this theory were critically examined by comparison with actual devices, mainly by the Purdue University group. This appears to have been the first occasion on which Log (I) versus V plots were used for analysis, and the work was probably the first systematic demonstration of the departures in the behavior of experimental diodes from accepted theories including the present ones. The form of typical results is shown in Figure 20. One sees two linear regions in the curve, with different slopes and corresponding different values of J_0 . These results showed that:

- (i) The theoretical value of α in Eq. (12) was too large by an amount varying from close to 1 to 4 or even more.
- (ii) Values of I_0 consistent with the forward characteristic were incompatible with the reverse characteristic.

The inconsistency between forward and reverse characteristics appears to have been due to barrier leakage, but the anomalies in α are still observed today, and will be further

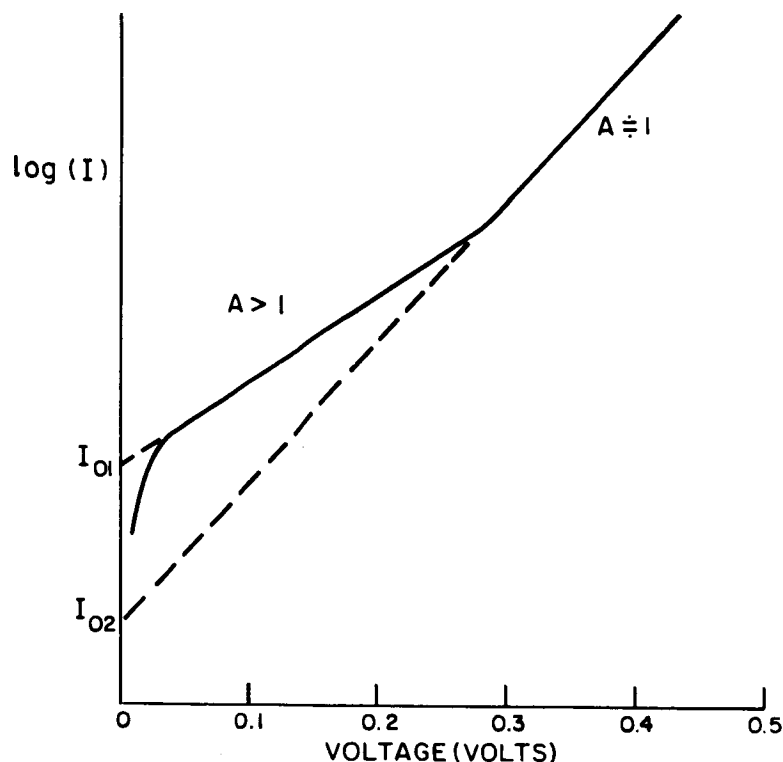


Figure 20. Log (I) vs. V for usual experimental diode

considered in later sections. Since this analysis concerns a device that is clearly not applicable to power generation, discussion has been limited to those aspects of the work which contributed to the progress of semiconductor junction theory.

b. Progress—1946 to 1955: During the war years, a great deal of experimental work was done at Bell Laboratories on the preparation of silicon and on fabrication of crystal diodes. After the war, this interest in crystal diodes was continued and led eventually to development of the transistor and the solar cell. The experimental work was the basis for significant advances in the theory which also came from Bell Laboratories, notably by Brattain, Barden, Shockley, and others.

Meyerhoff (159) conclusively established that for metallic contacts to n- and p-type silicon, the experimental facts did not fit the theory of the junction electrical properties. The disparity arose over the question of the relation between barrier height [V_0 in Eq. (18)] and the work function differences between the metal and the semiconductor. Whereas Brattain, as quoted by Bardeen (160), had found a correlation between work function difference and rectification for metal contacts evaporated onto cuprous oxide, Meyerhoff found no correlation between work function difference and barrier height, but rather, the same metal could make a rectifying contact to both n- and p-type silicon, only the direction of easy current flow being reversed by the semiconductor type change.

Bardeen (160) accounted for this behavior by considering surface states lying inside the forbidden band. Surface states are energy levels associated with the properties of a semiconductor surface, and are physically located there. They may or may not be associated with impurity atoms. Bardeen assumed the surface states to be both acceptor and donor type levels distributed over a range of energies in the forbidden band, but no assumption about the form of the distribution was made. Most of the donor levels lying above the Fermi level E_f will be vacant, and the remaining ions will provide a positive charge at the surface. Similarly, most of the acceptor levels lying below the Fermi level will be occupied by electrons, and will provide a negative charge at the surface. Acceptor levels above the Fermi level and donor levels below the Fermi level, will be largely un-ionized and thus electrically neutral. Hence, an energy E_0 may be defined for which, according to the Fermi function, the number of ionized surface donor levels above E_0 equals the number of ionized surface acceptor levels below E_0 , when the Fermi level would be at E_0 [see Figure 21(a)]. The magnitude of E_0 will therefore be determined by the distribution of the surface states. In thermal equilibrium, the Fermi energy must be constant throughout the material. To obtain this condition and simultaneously maintain overall charge neutrality in the semiconductor, bending of the valence and conduction bands in general occurs, as shown in Figure 21(b) for n-type material. This means that at equilibrium, the net surface charge (caused by $E_f \neq E_0$) is balanced by a charge near the surface due to ionized donors which are not compensated by free electrons. Thus a space charge region is created below the surface. For p-type material, the converse occurs. Now it is clear that if the density of surface states is high, the difference between E_f and E_0 need be very small regardless of the doping density and type of the semiconductor bulk. Hence, the band-bending, and particularly the barrier height V_0 , will be rather independent of the semiconductor properties, provided the surface state density is high, and the Fermi level in the semiconductor bulk is not near the center of the gap, which means that the semiconductor properties have to be strongly influenced by the donors or acceptors. By the same mechanism, when a metal-semiconductor junction is formed, creating a large density of surface states with rather uniform distribution, the Fermi level at the semiconductor surface need move by only a small amount to provide a surface dipole layer of sufficient magnitude to compensate for the difference in work functions of the metal and semiconductor. Thus, V_0 will again be only little affected by the work function of the metal, in correspondence with the experimental results of Meyerhoff.

It is interesting to note that Bardeen's paper appears to contain the first mention in a theoretical context of a junction between p- and n-type regions of the same material. This reflects the progress made in the preparation of semiconductors, since it was now possible for the first time to prepare a material with both conductivity types, and, hence, it became worthwhile to consider theoretically a p-n junction rather than a metal-semiconductor junction.

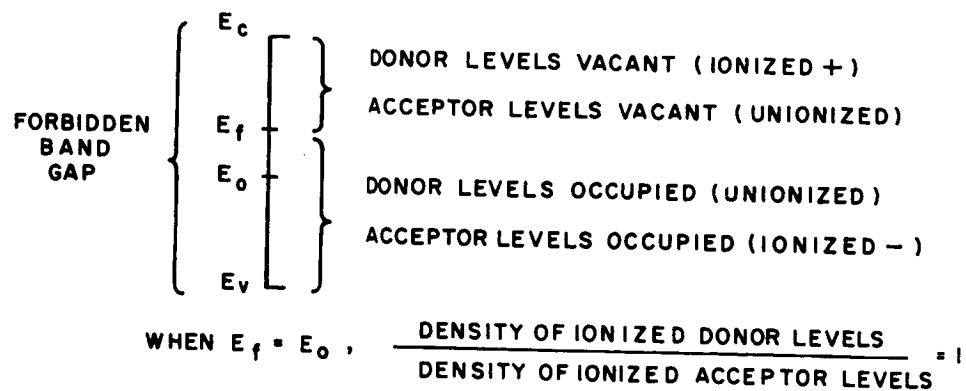


Figure 21(a). Energy levels at semiconductor surface

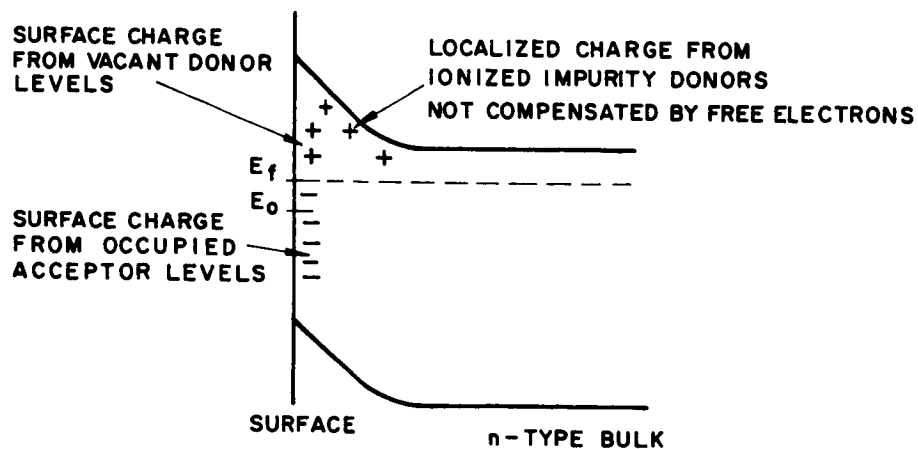


Figure 21(b). Formation of band-bending at semiconductor surface, after Bardeen

Sosnowski (132) appears to have been the first to publish results of an analysis of p-n junction behavior. However, Sosnowski considered the case of a very narrow junction region, with a transition region width less than the scattering length for carrier-lattice interactions. (Sosnowski's analysis is therefore to be contrasted with the results of Shockley, whose analysis concerned a junction sufficiently wide so that diffusion effects occurred in the junction region.) In the result of Sosnowski's theory the hole and electron currents followed the familiar exponential dependence on applied bias, leading to the rectifier characteristic. This analysis was performed to describe experimental effects seen in lead sulfide. The specimens were thin layers, with localized "excess" and "defect" characteristics, the p- and n-regions arising from oxygen impurity and excess lead, respectively. These specimens were photosensitive, and further mention of this work will be found in Section IV-E below.

The results of the most important theoretical work on p-n junction characteristics were published by Shockley in 1949 (161). As these results are the basis for much of the present understanding and viewpoints on p-n junction behavior, they will be considered in some detail.

The band structure of the semiconductor under consideration is shown in Figure 22,⁷ for various situations.

It is convenient to define an electrostatic potential ψ , midway between the valence and conduction bands. At thermal equilibrium, the hole and electron densities in the valence and conduction bands, respectively, are determined by the Fermi energy, and the electrostatic potential according to the expressions:

$$p = n_i \exp \frac{q (\psi - E_f)}{kT} \quad (20)$$

$$n = n_i \exp \frac{q (E_f - \psi)}{kT} \quad (21)$$

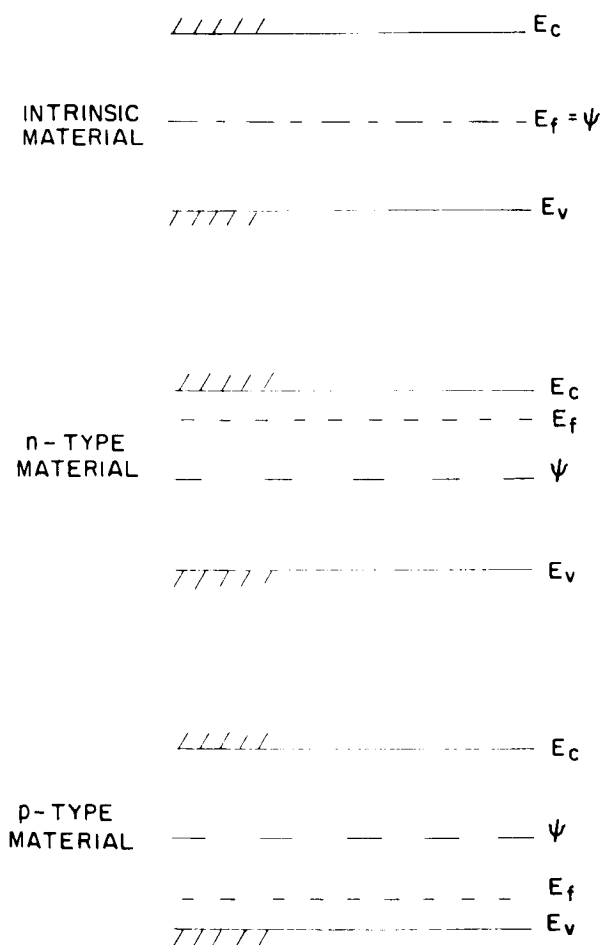


Figure 22. Band structures of semiconductor of various conductivity types

⁷To maintain consistency in this report, electron energy is plotted as increasing in the positive direction on the ordinate. Shockley's original diagram was plotted in the inverted sense.

where

- n_i = free electron density in intrinsic material
- n = free electron density in extrinsic material
- p = free hole density in extrinsic material.

One observes that Eqs. (20) and (21) apply for the "nondegenerate" case, where the Fermi function can be described by the Maxwell-Boltzmann distribution (see Section D-1 above). This provides commonality with Schottky's and Mott's work, and as before, the exponential I-V curve arises from this basic relationship. In the nonequilibrium case, existing, for instance, when excess holes are present in n-type material, the distribution of electrons and holes in the conduction and valence bands cannot strictly be described by a Fermi level.

However, in analogy to Eqs. (20) and (21), two separate quasi-Fermi levels can be used to describe the nonequilibrium densities of holes and electrons, as exemplified in Figure 23.

$$p = n_i \exp \frac{q (\psi - E_{fp})}{kT} \quad (22)$$

$$n = n_i \exp \frac{q (E_{fn} - \psi)}{kT} \quad (23)$$

Currents in the semiconductor may arise either from nonuniform carrier distribution (diffusion effects) or from electrostatic potential gradients (drift effects). Hence, the hole and electron currents are described by

$$I_p = q (D_p \nabla p - \mu_p p \nabla \psi) \quad (24)$$

$$I_n = bq (D_p \nabla n + \mu_p n \nabla \psi) \quad (25)$$

where

- μ_p = hole mobility
- D_p = diffusion constant for holes
- b = ratio of electron to hole mobility

Noting that

$$\mu_p = \frac{qD_p}{kT} \quad (\text{Einstein relation}), \quad (26)$$

Eqs. (24) and (25) can be rewritten using Eqs. (22) and (23):

$$I_p = q\mu_p p \nabla E_{fp} \quad (27)$$

$$I_n = qb\mu_p n \nabla E_{fn} \quad (28)$$

If it is assumed that all acceptors and donors are ionized, then the net charge density at a point in the semiconductor is

$$\rho = q(p - n + N_d - N_a) \quad (29)$$

where

$$N_d = \text{local donor density} \quad (30)$$

$$N_a = \text{local acceptor density}$$

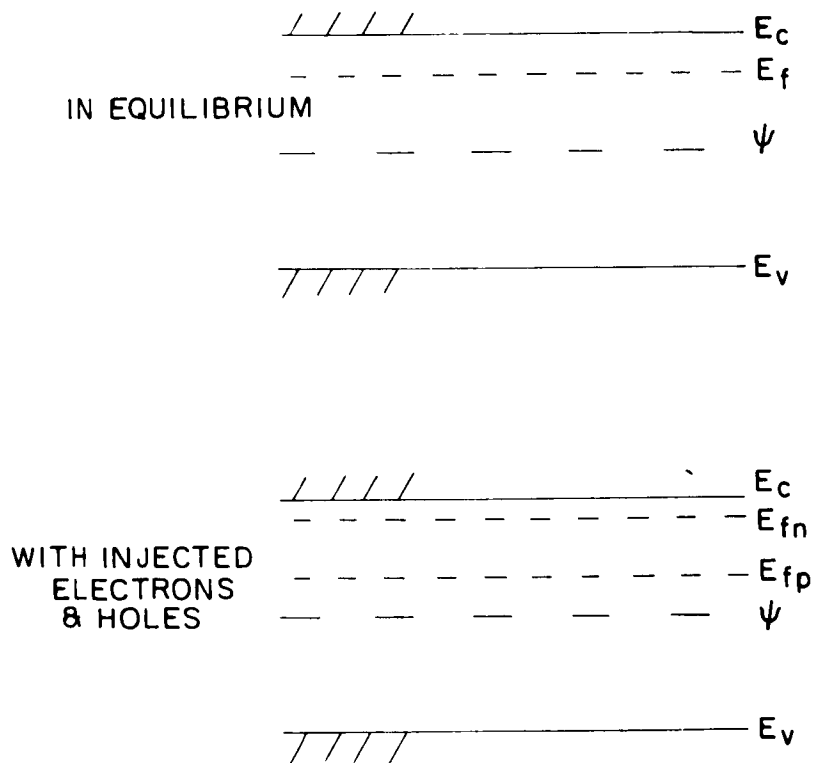


Figure 23. Energy levels in n-type semiconductor in thermal equilibrium, and with injected carriers

Considering a semiconductor in which the values of N_a and N_d are spatially varying, so that a junction between p- and n-type regions exists, Shockley showed that two cases can be obtained:

- (i) If N_a and N_d change sufficiently slowly in moving spatially through the material, the changes caused by ionization of the acceptors and donors are neutralized by the presence of balancing charges from the free carriers.
- (ii) If N_a and N_d change rapidly, then this charge balancing does not occur, and localized net space charge densities exist in the junction region.

It is convenient to set $E_f = 0$ under equilibrium conditions. Now Poisson's equation relates the charge density to the electric field:

$$\nabla^2 \psi = \frac{4 \pi \rho}{\kappa} \quad (31)$$

where

κ = dielectric constant

Substituting for ρ from Eq. (29), Eq. (31) can be integrated twice to yield the potential distribution in the junction region. Two boundary conditions are needed: one is applied by putting $\psi = 0$ at $x = 0$ (i.e., $x = 0$ is placed at the center of the junction, where $\psi = 0$ coincides with $E_f = 0$; see Figure 24). The second is applied by putting $(d\psi/dx) = 0$ at $x = x_m$, x_m being the edge of the space-charge layer, where ψ assumes the bulk equilibrium value. Hence, the width of the space-charge layer and the potential distribution in the layer are obtained in their dependence on the distribution of the fixed charges $N_d - N_a$. In deriving the junction I-V characteristic, Shockley assumed that the diffusion length for minority carriers is long compared with the transition region width. This is an important assumption which is not always fulfilled in actual devices, but which facilitates the following derivation by making the hole and electron currents remain uniform across the transition region, which extends between x_{Tn} and x_{Tp} , as shown in Figure 24, and serves to illustrate the case under consideration. He also assumed that the currents are sufficiently small so as not to alter significantly the minority-carrier lifetimes and diffusion constants outside the transition region. Shockley's derivation was done in such a way as to obtain both the dc and ac behavior (particularly the impedance) of the junction. For solar cell purposes, this is an unnecessary complication, so that attention shall be confined to the dc component.

The hole density at the point x_{Tn} under an applied bias $\delta\phi = (q/kT)\delta E_f$ is given by

$$p(x_{Tn}) = n_i \exp \left[\frac{q(\psi_a - E_{fa} - \delta E_f)}{kT} \right] \quad (32)$$

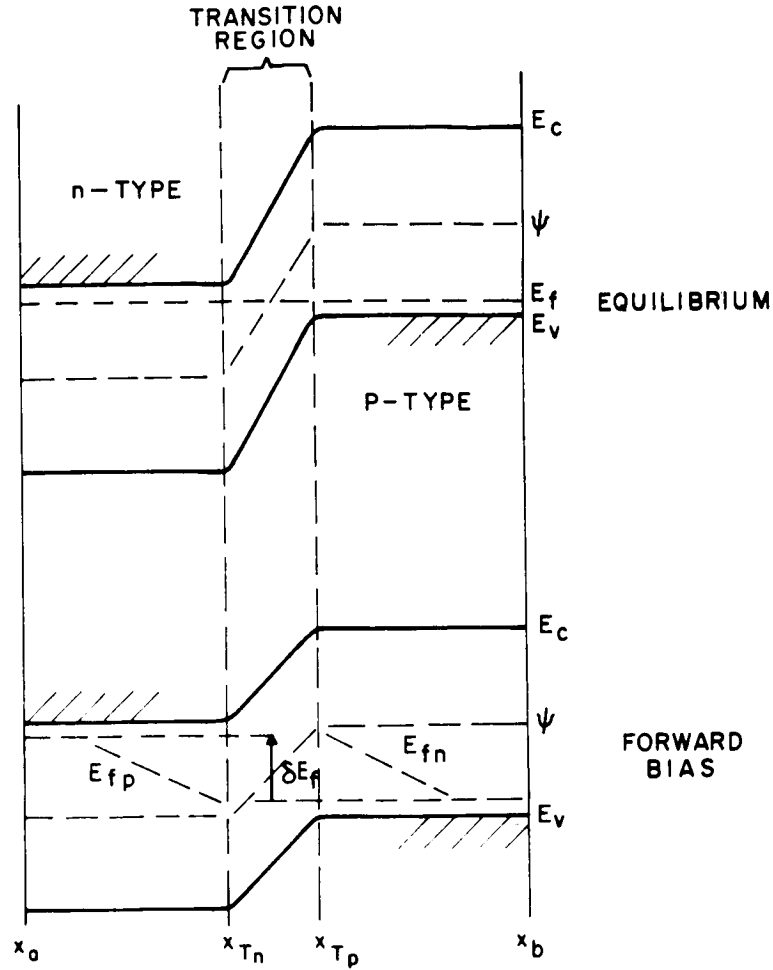


Figure 24. Band structure and energy levels in a p-n junction at equilibrium and under forward bias, after Shockley.

$$p(x_{Tn}) = p_n \exp \left(\frac{-q \delta E_f}{kT} \right) \quad (33)$$

where

x_{Tn} = edge of transition region

p_n = equilibrium hole concentration in the n region

$E_{fa} = E_{fn}$ at $x = x_a$

$\delta E_f = E_{fn} - E_{fp}$ in transition region and the subscript a denotes a value sufficiently far from the junction that the equilibrium values are obtained; see Figure 24. The hole current is carried by that part of $p(x_{Tn})$ which is in excess of the equilibrium value; i.e., the hole density carrying the hole current is

$$p_o(x_{Tn}) = p_n \left[\exp \left(\frac{-q \delta E_f}{kT} \right) - 1 \right] \quad (34)$$

Now the current carried by the holes is given by

$$I_p(x_{Tn}) = qD_p \cdot \frac{dp}{dx} \quad (35)$$

(dp/dx) is governed by the rate at which the excess holes (p_o) are removed by recombination according to the relation: $p = p_o \exp(-x/L_p)$ so that

$$\frac{dp}{dx} = \frac{-p_o}{L_p}$$

where L_p = diffusion length for holes in the n-region. Hence,

$$I_p(x_{Tn}) = \frac{qD_p}{L_p} \cdot p_o(x_{Tn}) \quad (36)$$

Placing ($x = x_{Tn}$) to obtain p_o at this point, and by similar considerations for the electron current, the total junction current is obtained:

$$I = I_p(x_{Tn}) + I_n(x_{Tn}) = qD_p \left(\frac{p_n}{L_p} + \frac{b n_p}{L_n} \right) \left[\exp \left(\frac{-q \delta E_f}{kT} \right) - 1 \right] \quad (37)$$

The junction equation can now be re-written in the familiar form

$$I = I_o \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] \quad (38)$$

where

$$V = -\delta E_f \cdot q$$

$$I_o = I_{po} + I_{no} = qD \left(\frac{P_n}{L_p} + \frac{b n_p}{L_n} \right) \quad (39)$$

By writing, according to Eqs. (20) and (21):

$$n_i^2 = p_n \times n_n = p_p \times n_p$$

$$I_o = qD_p n_i^2 \left(\frac{1}{L_p n_n} + \frac{1}{L_n p_p} \right) \quad (40)$$

Thus, I_o is seen to depend on the intrinsic carrier density n_i , and on the majority-carrier densities on the two sides of the junction. I_o thus is expected to decrease with increasing E_g (since this reduces n_i exponentially), and to decrease with increasing impurity density (n_n and p_p)

Shockley then showed that, if there exists a localized region of high recombination rate in the transition region, an ohmic component of conductance is added in parallel with the rectifying characteristic of the junction. This will be particularly noticeable in the reverse characteristic.

Assuming that (i) the ohmic contact to the p-region injects only holes, (ii) the ohmic contact to the n region injects only electrons, (iii) there is no recombination, and (iv) that the charges introduced into the specimen by changing the applied reverse-bias voltage, change only the charge distribution at the space charge region of the p-n junction, so that the direct current flow does not change across the latter, then the device behaves as a variable capacitor. Shockley derived expressions for the value of the capacitance for two cases: (i) the linearly graded junction, for which it was shown that $1/C^3$ is a linear function of applied voltage, and (ii) the abrupt junction (in which N_d and N_a are step functions at $x = 0$), for which $1/C^2$ is a linear function of applied voltage. The capacitance is the only junction parameter in Shockley's theory which is dependent on the detail of the junction structure, and, hence, provides an invaluable diagnostic approach to analysis of p-n junction geometries. It should be noted, however, that the assumptions used in the derivation limit the results to the case of reverse bias, and neglect the reverse saturation current.

Thus, Shockley provided an equation for the current which would be expected to flow in a device containing a p-n junction [Eq. (37)]. This showed that, provided:

- (i) the change in impurity concentration is sufficiently sharp, that local space charges occur;
- (ii) diffusion governs the motion of excess carriers in the material outside of the space-charge region [Eqs. (24) and (25)];
- (iii) the recombination of carriers in the transition region can be neglected (diffusion length is long compared with the transition region width); and

- (iv) the densities of injected charge carriers are small compared with the equilibrium values;

then the I-V characteristic of the device depends only on the values of the bulk material parameters included in Eq. (37), and does not depend on the detailed way in which the donors and acceptors are distributed in forming the junction.

It is interesting to consider why Shockley's analysis should have proved so valuable in later work. Naturally, the reasons lie largely in the analytical talents and experience brought to bear on the problem. Shockley had been working on solid-state theory from 1935 and is cited by Seitz as having made contributions to the latter's work. It also seems that the experimental work done during the war period at B.T.L., provided a good working knowledge of the likely values for the various materials parameters. This compilation of data on ionization energies of impurities, carrier densities, lifetimes, diffusion lengths, mobilities, and junction widths enabled appropriate approximations and simplifications to be made in the analysis. Thus, a balance could be struck between a rigorous treatment dealing with every conceivable process (which, even had it been possible, would have led to intractable solutions), and a solution so simplified as to be of little value.

Shockley's main contribution appears to have been the application of the solid-state band theories and the carrier transport equations to a particular physical situation, which approximates the generally occurring one satisfactorily. Shockley also provided a unification of existing ideas, giving a synoptic analysis which could be used as a starting point for later work in a wide variety of fields.

3. Theory of Photovoltaic Cells

a Photoeffects at p-n Junctions: During the 1930's, a primary interest in semiconductor research lay in the photoeffects which were seen in copper-copper oxide photocells. During this period, Schottky and others provided the basic theory of the photovoltaic effect, as discussed previously. In the period which followed, the major fields of interest for semiconductor research lay in the use of point-contact metal-semiconductor diodes for microwave applications, and later in transistor action. Thus, the major theoretical work was done on diode characteristics, with notable advances being made in p-n junction theory, an account of which has been given in the preceding section. Although it was well established that p-n junctions were photosensitive, very little work was done in this area until experimental work on single-crystal silicon solar cells indicated that the photovoltaic effect could have application to power generation. Work on the photovoltaic effect and the theory and analysis of devices using the effect then proliferated. It should be realized, however, that all of these analyses were based on the concepts developed during the early work on copper oxide cells, even though many

of those involved appear to have been unaware of this. The account which follows describes the progress of the theory of the photovoltaic effect, and the next section of this report describes the progress of device analysis.

As described in Section III-C-2 of this report, Ohl and others at Bell Telephone Laboratories had observed photosensitivity at p-n junctions in silicon about 1940. However, this observation appears to have not been reported at the time, nor was it followed up during the wartime work. Hence, it appears that Sosnowski, Starkiewicz, and Simpson, working at the Admiralty Research Laboratory in England, were the first to report a photoeffect which was positively identified as occurring at a p-n junction (162-164). The specimen was lead sulfide, rendered p-type by oxygen impurity and n-type by excess lead, and the junctions occurred at the grain boundaries in thin layers used as infrared-sensitive photoconductors. The phenomena were explained by an energy band diagram for the p-n junction as shown in Figure 25, which is close to presently accepted ideas. The mechanism proposed for the photovoltaic effect was that electrons are transferred from the ground state to the conduction band, diffuse across the barrier, lose energy by collision with the lattice and are thus prevented from returning across the barrier.

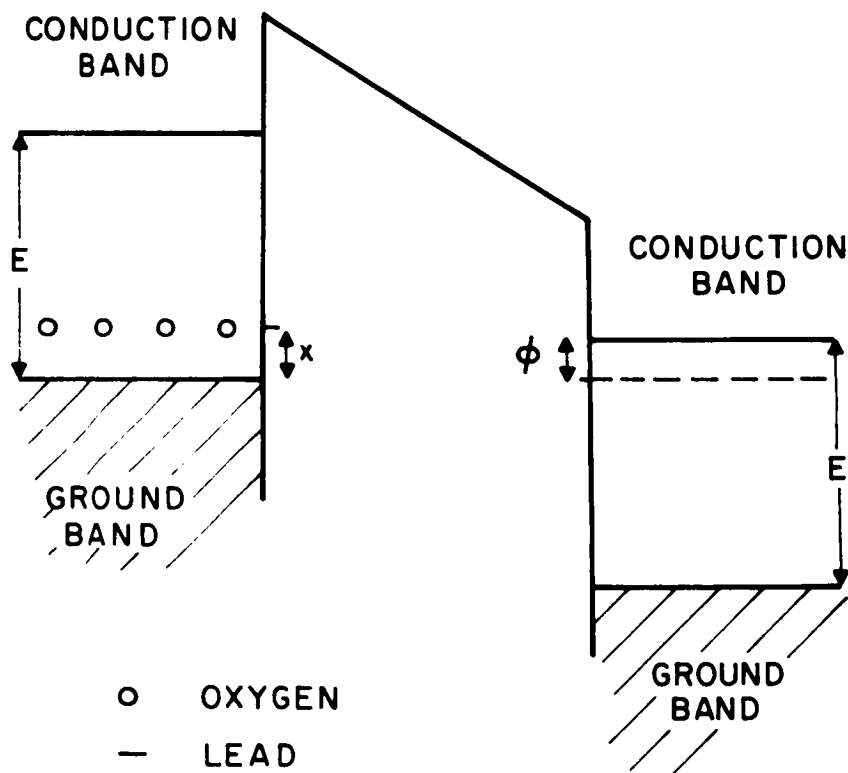


Figure 25. Junction structure in PbS, after Sosnowski et al.

This hypothesis was checked against experiment for direction of the photovoltage, and found to be correct. No quantitative analysis was reported, though an analysis of the I-V characteristic of the junction was provided, as described above. The important point of this work was the p-n junction band structure, which followed from earlier work, and probably had been used previously, but which had not appeared in the literature before.

In 1948, Lehovec published the results of theoretical work aimed at giving a comprehensive description of the photovoltaic effect in metal-semiconductor junction cells (1.29), building on the results of Schottky and Mott. The assumptions underlying the analysis were:

- (i) An "effective barrier layer width" can be defined in a metal-semiconductor junction cell, and only carriers released in this region contribute to external current. This region may be approximately equal to the barrier region width determined by capacitance measurements.
- (ii) Both drift and diffusion contribute to carrier motion.
- (iii) Recombination in the active region may be neglected because free carrier densities are low in this region.
- (iv) Absorption of a photon creates both free electrons and free holes, and these behave in exactly the same way as thermally generated free carriers.

Equating the density of carrier generation (using the exponential fall-off of light intensity with distance-Lambert's law) with the rate of change of current density with distance [right-hand side of Eq. (41)]:

$$\frac{J}{h\nu} \cdot \alpha \cdot \beta \exp(-\alpha x) = -\frac{1}{q} \frac{d}{dx} \left(-nq\mu_n \frac{dV}{dx} + qD_n \frac{dn}{dx} \right) \quad (41)$$

where

- J = illumination intensity
- $h\nu$ = energy per photon
- α = optical absorption constant
- β = number of electrons released per photon absorbed
- x = distance coordinate
- μ_n = electron mobility
- D_n = electron diffusion constant

This equation was solved to give a general "equation of state":

$$\left(\frac{Jq}{h\nu} \right) \cdot \beta A + I = n_o q \mu F \left[\exp (qV/kT) - 1 \right] \quad (42)$$

with

$$A = \frac{1}{\left(1 + \frac{\alpha kT}{qF} \right)} - \exp (\alpha d)$$

and

F = absolute value of field intensity at $x = 0$

$$V = V_o + \frac{kT}{q} \ln \left(\frac{n_d}{n_o} \right)$$

V_o = barrier height

n_o = electron density at $x = 0$

n_d = electron density at $x = d$

d = "effective thickness" of barrier layer

I = current

Equation (42) has the general form of the presently used equation for the description of the solar cell characteristics. The first term of the left-hand side of Eq. (42) represents the light-generated current, the right-hand side the diode current. Lehovec pointed out that A effectively governs the quantum yield of the device. $A = 1$ is obtained if all incident quanta are absorbed in the active region, and all electrons generated are collected.

Working from Eq. (42), Lehovec showed that:

- (i) The predicted photovoltage and photocurrent directions agreed with experiment for both p- and n-type semiconductors.
- (ii) For $J = 0$, the dark dc characteristic of the device was given.
- (iii) The short-circuit current (I_{sc}) was directly proportional to the light intensity.
- (iv) The open-circuit voltage (V_{oc}) was proportional to J for $V \ll kT/q$, and proportional to $\log (J)$ for $V > kT/q$.

Although these results had been obtained before by separate analyses, Lehovec's major contribution was to derive all of these major device characteristics from a unified starting point.

Lehovec also pointed out that it is useful to consider a maximum power point on the characteristic curve, and that an approximation to the maximum available power (P_{\max}) is the $V_{oc} \times I_{sc}$ product, though this will be higher than the actual value. It was also pointed out that P_{\max} increases as (J^2) at very low light intensities ($V_{oc} \ll kT/q$), and as $J \times \log(J)$ at high light intensities ($V_{oc} > kT/q$).

The most important points made by Lehovec were:

- (i) The photons must create free carriers of both types if an external current is to be obtained.
- (ii) Consideration of a maximum power point is useful.

Because of the changing technology, interest then moved to p-n junctions, and germanium devices were studied almost exclusively during the 1949-54 period. In 1949 and 1950, Fan (165) and Becker (134) reported work on germanium p-n junction devices, in which the open-circuit voltage V_{oc} was described by

$$V_{oc} = \frac{kT}{q} \ln \left(1 + \frac{\Delta n_p}{n_{po}} \right) \quad (43)$$

where

n_{po} = unilluminated (equilibrium) free electron density
 Δn_p = excess electron density generated by light

This predicted open-circuit voltage was compared with experiment. Since the device was illuminated at the edge of the junction only (the junction was normal to the exposed face), various extraneous effects were introduced (shunting by the unactivated junction, leading to high temperature sensitivity, and surface recombination effects).

A more advanced germanium p-n junction device was investigated by Ruth and Moyer (140) and reported in 1954. Here a grown junction was parallel to and about 0.1 mm below the exposed surface. Experiments which measured the power conversion efficiency of the device confirmed in general the theoretical analysis of Lehovec, showing that the efficiency increased proportionally to the light intensity under low illumination, and as the logarithm of the illumination at higher illumination levels. A theoretical analysis of the current-voltage characteristic and of the photovoltaic performance of this device was performed and published early in the same year by Cummerow. A review of this work is presented in the Section III-D-3-b.

Rothlein and Fowler (138) also presented a theoretical analysis of a germanium photovoltaic cell with a junction formed by alloying. The analysis was based on established concepts, and applied to a device type which is no longer of general interest for power conversion.

The publication of the results from the Bell Laboratories work on diffused silicon cells included a number of similar analyses occurring about the same period, and present-day discussions on the photovoltaic effect also often include a similar analysis. Both the equivalent circuit and the derived expressions for I-V characteristics are fundamentally similar to the work done by Schottky during the early 1930's. An analysis of both the electron-voltaic and the photovoltaic effects was given by Pfann and van Roosbroeck (141) in 1954.

The equivalent circuit used is shown in Figure 26. (In the following the symbols and some of the current directions have been altered to make them consistent with the rest of this report.) Then

$$I = I_D - I_L \quad (44)$$

$$I_D = \left(\frac{kT}{qR_o} \right) \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] \quad (45)$$

where

$$R_o = \frac{kT}{qI_o} = \left(\frac{dV}{dI_D} \right)_{V=0}$$

R_o is the zero-point resistance of the diode, directly related to the saturation current.

$$V = -IR_L \quad (46a)$$

and the power output

$$P = IV = I^2 R_L \quad (46b)$$

To find the load resistance giving maximum power (R_L'):

$$\frac{dP}{dR_L} = 0 \quad (\text{at optimum load})$$

and hence,

$$I_L = \left(\frac{kT}{qR_L} \right) \ln \left(\frac{R_o}{R_L} \right) + \left(\frac{kT}{q} \right) \left(\frac{1}{R_L} - \frac{1}{R_o} \right) \quad (47)$$

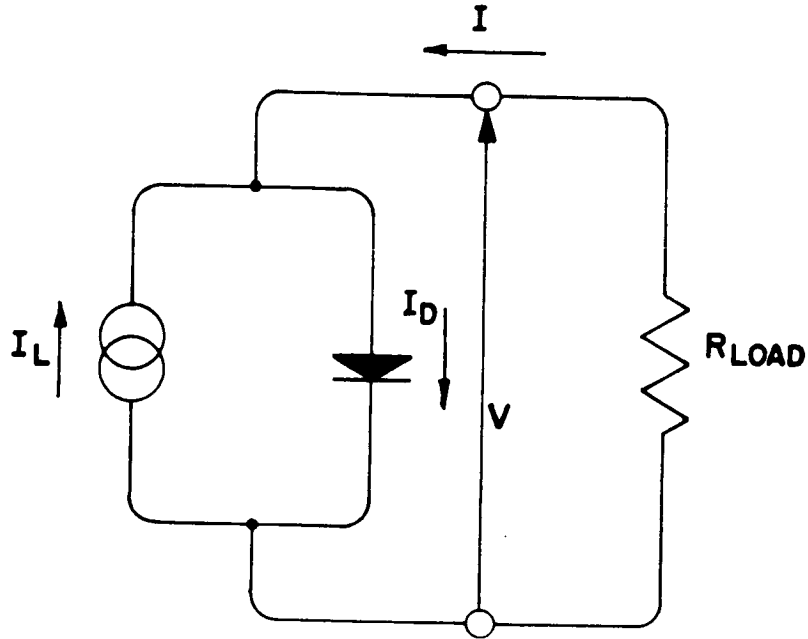


Figure 26. Simplified equivalent circuit of a photovoltaic cell

Equation (48) is based on the cell equivalent circuit which neglects R_s and R_{sh} (as shown in Figure 26), and it is assumed that the diode characteristic obeys Shockley's diffusion theory. Equation (47) must be solved numerically to obtain R_L' .

Pfann and van Roosbroeck then provided a series of manipulations to simplify the resulting relationships. Thus, they obtained an expression for the maximum power available, in terms of the optimum load resistance:

$$P_m = \frac{1}{R_L'} \left(\frac{kT}{q} \ln \frac{R_o}{R_L'} \right)^2 \quad (48)$$

Pfann and van Roosbroeck also provided an analysis of the effect of recombination in reducing the light-generated current, by introducing a factor Q , for quantum efficiency of the cell, defined as the ratio:

$$Q = \frac{\text{number of hole-electron pairs separated by the p-n junction}}{\text{number of photons absorbed in the semiconductor}}$$

An expression for Q in terms of the junction depth, the surface recombination velocity, the optical absorption constant for the semiconductor, and the diffusion lengths in the p- and n-regions, was then given, without derivation, for the case of an infinite base thickness, with collection based on diffusion only. This appears to be the first detailed analysis of the quantum efficiency or collection efficiency, as it was called later by some authors, based on semiconductor material properties.

The significance is the realization by these authors, without their stating it, that the light-generated current density, or the collection efficiency, can be analyzed separately from the current-voltage characteristic of the device, based on the linear superposition of the current. These authors had to solve the same continuity equation which Cummrow used slightly earlier, but the analysis of light generated current only, provided simpler boundary conditions and easier manipulation of the solutions. Thus this analysis set the model for later theories, which included refinements to approximate the actual devices more closely.

Pfann and van Roosbroeck also noted that germanium junctions generally follow the theoretical diode equation with $A = 1$:

$$I_D = I_0 \left(\exp \frac{qV}{AkT} - 1 \right) \quad (49)$$

However, they noted that silicon junctions frequently show values of $A > 1$.

Thus, by the end of 1954, the fundamental analyses of both the junction characteristic and the photovoltaic effect in a p-n junction device were well established. Work from 1955 to the present time has refined these basic results and shown how various imperfections in the cells contribute to losses in conversion efficiency.

b. Ultimate Conversion Efficiency: The photovoltaic germanium p-n junction device of Ruth and Moyer, which showed a sunlight conversion efficiency approaching 1%, stimulated Cummrow (who was working in the same laboratory of the General Electric Company), to analyze theoretically the maximum power conversion efficiency achievable with a germanium device (166). The geometry of the device considered is shown in Figure 27. The illumination generates hole-electron pairs in the semiconductor, but it was assumed that the rate of generation is not sufficient to substantially alter the majority-carrier density on either side of the junction. It was also assumed that the width of the transition (space-charge) region of the junction is much less than the diffusion length of minority carriers, and also much less than $(1/\alpha)$, the characteristic optical absorption length in the material.

The Shockley-Read theory of recombination (a brief account is given in Section IV-A-1) was then applied to determine the net rate of generation of carriers, accounting for thermal generation, photon-absorption generation, and recombination through trapping levels. This net generation was then equated to the spatial rate of change of current,

which was assumed to occur only by diffusion. This resulted in the general continuity equation:

$$g_p + g(x) - \left(\frac{p}{\tau_p} \right) + D_p \frac{d^2 p}{dx^2} = 0 \quad (50)$$

for holes in the n-type region, where

- g_p = rate of thermal generation of holes in the n-type region
- $g(x)$ = rate of hole generation by light absorption in the n-type region
- p = nonequilibrium hole concentration in the n-type region
- x = spatial coordinate
- D_p = diffusion constant for holes in the n-type region.

Now light absorption in the semiconductor will be spatially dependent; hence,

$$g(x) = g_0 \exp(-\alpha x) \quad (51)$$

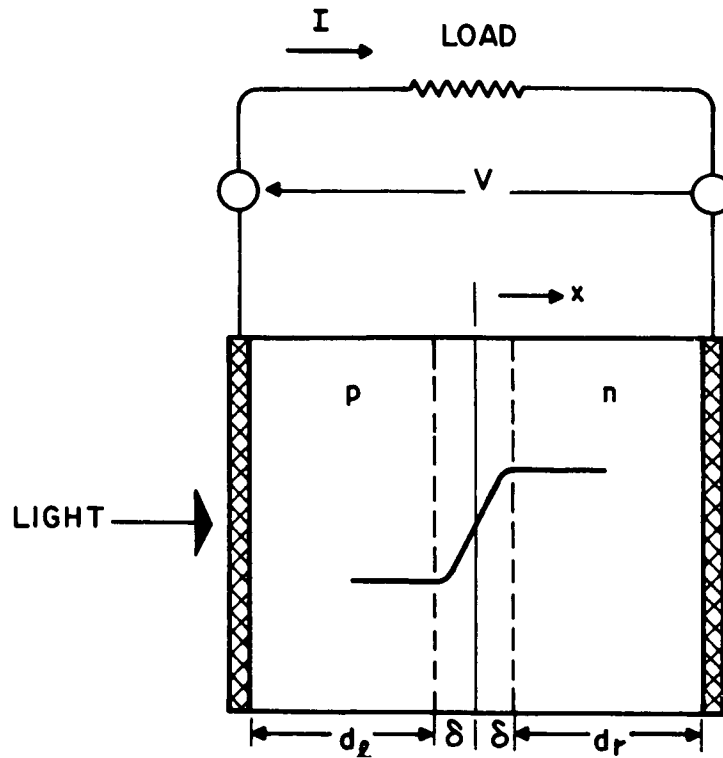


Figure 27. Photovoltaic junction geometry, after Cummertow

where

g_0 = rate of generation at $x = 0$
 α = optical absorption constant of semiconductor

If H_S photons $\text{cm}^{-2} \cdot \text{sec}^{-1}$ fall on the surface plane of the semiconductor, located at $x = -d_\ell$ after reflection by or absorption in the surface electrode have occurred, then the generation rate at $x = 0$ is:

$$g_0 = \alpha H_S \exp(-\alpha d_\ell) \quad (52)$$

Equations (51) and (52) were substituted into Eq. (50), which was then solved with boundary conditions suitable for a particular device geometry; e.g., for a device with either infinite thickness of the base and surface regions, or a device with finite thickness of both regions, but with zero surface recombination velocity at these surfaces⁸. The boundary conditions were:

$$p = p_n \exp\left(\frac{eV}{kT}\right) \text{ at } x = 0 \quad (53)$$

$$\frac{dp}{dx} = 0 \text{ at } x = d_r \text{ and } x = d_\ell \quad (54)$$

or

$$\lim_{d_r \rightarrow \infty} p = p_n \quad (55)$$

where

p_n = equilibrium hole concentration in the n-region.

Cummerow then integrated Eq. (50) to provide p as a function of x and V , and obtained the hole current crossing the junction by applying

$$I_p(0) = -q D_p \left(\frac{dp}{dx}\right)_0 \quad (56)$$

⁸Cummerow quoted Hall as a source for this assumption, which appears to be based on the reflection of minority carriers by an $n-n^+$ junction. Although this reflection is possible in principle, it appears that in practice it is not sufficiently strong to prevent recombination at ohmic contacts, and an assumption of infinite recombination velocity at such contacts together with finite recombination velocity at the free front surface has been used by subsequent workers.

where

$$I_p(0) = \text{hole current at } x = 0$$

A corresponding derivation provided $I_n(0)$, the sum of the electron and hole currents then constituting the total junction current as a function of V . Hence, it was found that

$$I = q g L' \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] - q g_o L \quad (57)$$

where L and L' are lengths related to the combined effects of the diffusion lengths for minority carriers on the two sides of the junction, g_o is the generation density rate for hole-electron pairs at the junction by photon absorption, and g is a term containing the sum of the thermal generation density rates for minority carriers on both sides of the junction. The first term on the right-hand side is consistent with Shockley's expression for the characteristic of diodes based on diffusion and recombination of injected carriers on both sides of the transition region, as discussed in Section III-D-2 above, while the second term gives the light-generated current for the case of not quite realistic boundary conditions.

Thus, Cummrow was the first to publish a comprehensive analysis of the photovoltaic effect in pn-junction devices in a valid approach, although it was more cumbersome than necessary because of the inclusion of the diode characteristic.

Cummrow then derived expressions for the maximum power delivered to an external load, by straightforward circuit analysis. He proceeded to calculate the theoretical efficiency by introducing measured material constant values appropriate for germanium. These included the minority-carrier diffusion lengths and lifetimes, the equilibrium majority-carrier densities, and one value of optical absorption constant, corresponding to monochromatic illumination. The results showed an efficiency increasing with increasing junction depth to a broad maximum for $d_j = 0.002$ - 0.004 cm, and increasing monotonically with increasing illumination level, with $\eta \approx 23\%$ at $0.002 \text{ W} \cdot \text{cm}^{-2}$ and $\eta = 40\%$ at $1 \text{ W} \cdot \text{cm}^{-2}$ for $0.01 \text{ ohm} \cdot \text{cm}$ material, under monochromatic $1.5\text{-}\mu\text{m}$ illumination. Cummrow also showed that increasing the device temperature decreases the conversion efficiency by dropping the working voltage, using the results for the junction characteristic.

Later in the same year, after the publication of the performance data for diffused-junction silicon cells by the Bell Laboratories group, Cummrow extended this original analysis to consider material constants appropriate to silicon (167), and to include an integration over the 5760°K blackbody spectrum in place of monochromatic illumination, using absorption coefficient data as a function of wavelength as published previously by Moss (168).

For material with

$$\begin{aligned}\mu_n &= 1200 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1} & \sigma_n &= \sigma_p = 1.0 \text{ Ohm}^{-1} \\ \mu_p &= 400 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1} & \tau_n &= \tau_p = 10^{-5} \text{ sec}\end{aligned}$$

the efficiency obtained was 17%, neglecting optical reflection from the front face.

Cummerow, in his first paper, also pointed out that increased efficiency could be obtained by using highly doped material (provided the carrier mobility was not seriously impaired), and he also felt that material with an energy gap close to the peak of the solar intensity distribution curve would give the highest theoretical efficiency. Thus, he recommended use of a semiconductor with an energy gap near 2.0 eV, larger than that of silicon.

This question of the optimum bandgap for solar energy conversion efficiency has since been of considerable theoretical interest. The point touched on by Cummerow was taken up in more detail by Rittner, also in 1954 (169). Rittner used an analysis similar to that of Cummerow, and plotted conversion efficiency as a function of forbidden bandgap for several carrier densities in the range $N_a = N_d = 10^{15}$ to 10^{19} cm^{-3} . For materials with E_g greater than that for silicon, mobility and lifetime values equal to those of silicon were assumed. The efficiencies shown were those obtained with a junction at the optimum depth. The results indicated that the optimum bandgap for solar energy conversion lay around 1.5 - 1.6 eV, and that this would give a maximum efficiency of about 25% for $N_d = 10^{19} \text{ cm}^{-3}$. Hence, Rittner proposed the use of AlSb as a promising material for solar energy conversion.

Pfann and van Roosbroeck, working from their photovoltaic effect analysis as described in Section III-B-3, provided an estimate of maximum theoretical efficiency for a silicon solar cell operating under earth-surface sunlight. The spectral distribution of sunlight as published by the Smithsonian Institute⁹ was reduced to $89 \text{ mW} \cdot \text{cm}^{-2}$ to correspond to a solar elevation angle of 60° from the zenith for an average cloudless day at sea level, and used to calculate the maximum $I_L = 40 \text{ mA} \cdot \text{cm}^{-2}$. For this calculation, they neglected surface reflection loss and assumed each photon with energy $h\nu > E_g$ for silicon to create a hole-electron pair, as well as a collection efficiency of unity. Taking a value of $R_0 = 10^8 \text{ ohm} \cdot \text{cm}^2$ (calculated from experimental junction measurement) an efficiency of 18% was calculated to be the maximum theoretically achievable for a cell of this type.

Thus, by the end of 1954, the fundamental analyses of both the junction characteristic and the photovoltaic effect at a p-n junction were well established. Work from 1955 to the present time has refined these basic results, and shown how various imperfections in the cells contribute to losses in conversion efficiency.

⁹Smithsonian Meteorological Tables, 6th Rev. Edition, Table 131, (The Smithsonian Inst., Washington 1951).

E. THE ELECTRON-VOLTAIC EFFECT AND RADIATION DAMAGE

1. Semiconductor Damage and Annealing Studies

The first studies of the effects of high-energy particle bombardment on the electrical properties of germanium and silicon were performed by K. Lark-Horovitz et al. (170, 171). This work was performed at Purdue University and Oak Ridge National Laboratories. The Purdue work was initiated around 1947 under the support of a Signal Corps contract (172). Samples of p- and n-type semiconductor materials were bombarded with 10-MeV deuterons and 20-MeV alpha particles as well as neutrons. The results of the germanium studies indicated that the conductivity of p-type material tended to increase under irradiation, while that of n-type material decreased or converted to p-type. This was found to be true in germanium for all of the types of bombarding particles used. Deuteron-induced lattice defects were found to anneal out under prolonged heating at 400°C, while those caused by neutron bombardment were not so readily removed. Two years after the publication by Lark-Horovitz et al., W. H. Brattain and G. L. Pearson published an account of their studies on the effects of alpha particle bombardment on n-type and p-type germanium (173). They found essentially the same trend as the earlier workers, with conduction electrons being removed from n-type material at a rate of 78 electrons per alpha particle. After the material had been converted to p-type, holes (i.e., acceptors) were introduced at a rate of 8.6 per alpha particle. Some room-temperature annealing was observed. The results were found to agree fairly well with the theoretical predictions of Seitz. The first electron bombardment studies were performed by E. Klontz and K. Lark-Horovitz (174) using 0.7 to 2.0-MeV electrons to irradiate germanium, with results qualitatively similar to those found in the other studies. There were numerous other studies, both theoretical (175) and experimental (176), dealing with bombardment and annealing. The large majority of these were concerned with germanium, and only occasionally was silicon investigated, while Cleland and Crawford (177) published some data on indium arsenide which showed p-type InAs to be converted to n-type by neutron bombardment.

These studies were not intended to relate directly to the effects of radiation on photovoltaic or other devices although some of them were performed on semiconductor diodes. The discovery and investigation of the electron-voltaic effect, however, brought about a direct confrontation between the photovoltaic cell and radiation damage long before the discovery of the Van Allen radiation belts.

2. The Electron-Voltaic Effect

The electron-voltaic effect is the production of a current and voltage at a p-n junction as a result of bombarding the semiconductor containing the junction with beta particles (see Figure 28). It is the analog of the photovoltaic effect, with the difference that the electrons take the place of the photons. In this case each electron ionizes a number of atoms, giving rise to an electronic "gain". The observation of an electron-voltaic effect was first made by Ehrenberg, Lang, and West (178) in 1951, using selenium and

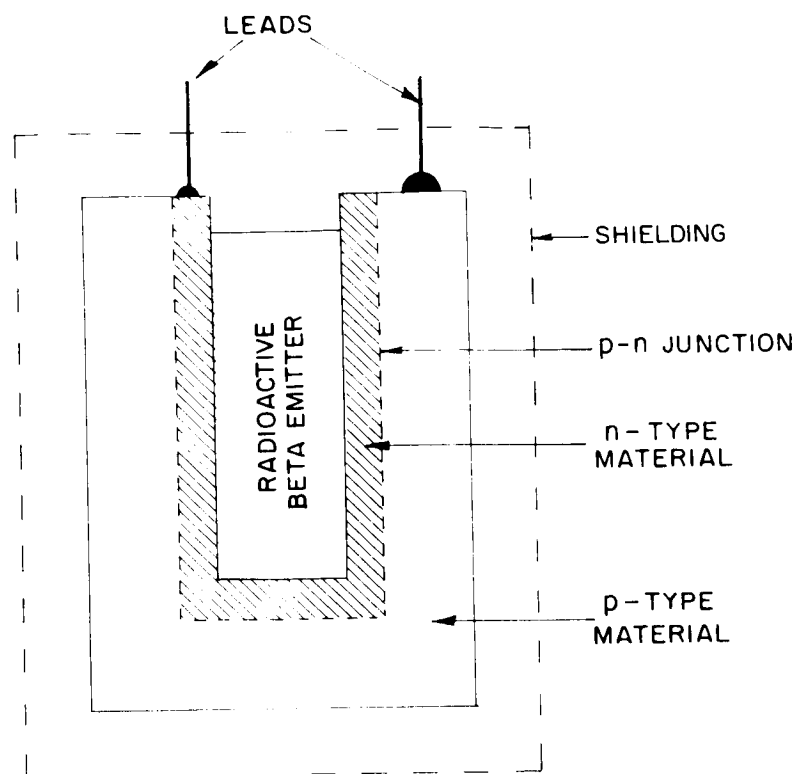


Figure 28. Schematic of electron-voltaic cell

copper oxide photovoltaic cells. The selenium cell was bombarded with a stream of electrons whose energy could be varied between zero and 80 keV. The maximum current gain was obtained with 50-keV electrons. Using a bombarding current density of approximately $10^{-8} \text{ A}\cdot\text{cm}^{-2}$ a gain (i.e., the ratio of electron-voltaic to bombardment current) of 500 was obtained for the electron-voltaic current at 50 keV and with a load of 700 ohms. The gain was found to be lower when higher bombardment currents were used. The energy dependence of the gain was thought to correlate with the penetration depth, and thus was dependent on device characteristics through the collection efficiency. To measure the effect on copper oxide cells, the authors found that it was necessary to remove some of the oxide layer. The threshold energy for observation of the electron-voltaic effect with the copper oxide cell was about 60 keV. From this point the gain increased with electron bombardment energy, reaching a value of 150 at 90 keV. These results were interpreted to indicate that the sensitive region of the copper oxide photocell was at the copper-copper oxide interface.

The first published account of the electron-voltaic effect in silicon and germanium was given by Rappaport early in 1954(179). Working under an Air Force contract, Rappaport used alloy junctions on germanium and silicon wafers with a 50 millicurie $\text{Sr}^{90}\text{-Y}^{90}$ radioactive source (average beta particle energy 0.7 MeV) for bombardment. The silicon p-n junctions gave a maximum open-circuit voltage of 250 mV and a short-circuit

current of 10^{-5} A. This corresponded to a current gain of 1.5×10^5 (beta current was 3.2×10^{-10} A), giving a "cost" figure for carrier production of 4.7 eV per charge carrier. Used as an energy conversion unit in conjunction with a radioactive source with an available power of 200 μ W, a single silicon junction gave an output of 0.8 μ W into a matched 10,000-ohm load - an efficiency of 0.4%. Based on calculations for a wafer of optimum thickness, an efficiency of 2% was predicted.

Factors other than wafer thickness lowering the efficiency were high reverse saturation currents, bulk and surface recombination, backscattering, etc. Using the same source with germanium an open-circuit voltage of 30 mV and a short-circuit current of 2×10^{-5} A were obtained. The current gain was 1.9×10^5 , with a "cost factor" of 3.7 eV per charge carrier. One of the junctions was used to power a transistorized audio oscillator. Such a power supply was expected to have a potentially long life; however, radiation damage effects were being noted which, it was felt, would tend to limit this lifetime. Later in the same year, Rappaport reported some results which confirmed, rather dramatically, this anticipation(180). He had found that the open-circuit voltage of the electron-voltaic cells could drop by as much as a factor of two during a 1-hour exposure to the 50 milli-curie Sr^{90} - Y^{90} beta source. This exposure was determined to correspond to a change in the number of defects present by 10^{11} cm^{-3} . As a result of these observations and of changes observed in the rectifier characteristics, it was concluded that minority-carrier lifetime is extremely sensitive to radiation damage.

During the same year, Pfann and van Roosbroeck published the independent work dealing with both the photovoltaic and electron-voltaic energy conversion capabilities of p-n junctions (141), which was discussed in Section III-D-3. Silicon electron-voltaic cells were shown to be more efficient than germanium cells, both theoretically and experimentally. An estimate of the theoretical idealized efficiencies gave a figure of 2.4% for silicon and 0.034% for germanium. Germanium, however, has a higher threshold (0.63 MeV) for radiation damage than silicon (0.3 MeV). A silicon electron-voltaic cell showed a decrease of 45% in short-circuit current over a two-day period of operation. Some of this damage tended to anneal out, and after five weeks at room temperature the short-circuit current returned to 62% of its original value. The possible use of absorbers to provide partial or total protection was considered but the reduction in efficiency associated with this protection was considerable. For the case of the complete protection, the ideal overall efficiency was calculated to be reduced to 5.8×10^{-7} percent (germanium).

In 1959 Loferski and Rappaport published some preliminary work relating lifetime and short-circuit current changes to the properties of the defects (181). They developed an expression connecting short-circuit current with bombardment time. Using this expression in analyzing their experimental data, Loferski and Rappaport determined that the energy, $E_{L_{\min}}$, necessary to displace an atom irreversibly from its normal position was, in the case of germanium $E_{L_{\min}} \leq 23 \text{ eV}$, and in the case of silicon $E_{L_{\min}} \leq 27.6 \text{ eV}$.

A comprehensive discussion of the results of this work on the electron-voltaic effect was given by Rappaport et al. in an additional publication (182). Although the electron-voltaic cell has not proven useful for present-day applications because of various factors such

as weight, lifetime, and efficiency, these early studies led to a fundamental understanding of the nature and effects of radiation damage in semiconductor devices and, in particular, in the electron-voltaic cell which is structurally very similar to the photovoltaic cell. This knowledge was to prove extremely valuable later when the advent of the space age brought large-scale application of photovoltaic cells in space, where they were exposed to radiation, predominantly from the then discovered radiation belts surrounding the earth.

IV. CONTEMPORARY DEVELOPMENTS (1955-PRESENT)

GLOSSARY OF SYMBOLS FOR SECTION IV

a	rate constant in emission process	J_{sc}	short-circuit current density	$R(V)$	rate of recombination of hole-electron pairs by non-radiative processes
A	empirical constant in the diode equation	k	Boltzmann's constant	S	aperture width in grid
c	velocity of light	L_o	minority-carrier diffusion length	t	diffused region thickness
E_A	acceptor energy level	$I(\nu)$	ratio of incident flux to flux emitted by a black body at the device temperature (function of frequency)	T	absolute temperature, or grid line width, in context
E_B	barrier height	m	path length of sunlight through atmosphere, referred to normal incidence	T_c	cell absolute temperature
E_c	energy at bottom edge of conduction band	m^*	effective mass of electrons or holes	T_s	sun temperature
E_f	Fermi level energy	n	electron density	T_l	black-body absolute temperature giving spectral distribution closest to solar spectrum
E_{fi}	intrinsic Fermi energy	n_i	free electron density in intrinsic semiconductor material	U	net rate of change of electron or hole density
E_{fn}	quasi-Fermi level energy for electrons	n_p	equilibrium electron concentration in the p region	U_{en}	net rate of change of electron density
E_{fp}	quasi-Fermi level energy for holes	n_{pn}	majority carrier density	U_{cp}	net rate of change of hole density
E_{ft}	quasi-Fermi energy for trap occupancy	n_n	electron concentration in n region at equilibrium	V	voltage
E_g	width of forbidden band-gap	n_o	equilibrium electron concentration	V_{Ga}	localized energy level arising from presence of gallium atom
E_{geub}	energy gap of cubic material	n_1, n_2	ionized impurity concentrations	V_m	maximum-power-point voltage
E_{ghex}	energy gap of hexagonal material	n_l	electron density in conduction band when $E_{fn} = E_t$	V_{oc}	open-circuit voltage
E_t	energy level of trap	N	energy flux, or photon flux, in context	V_p	localized energy level arising from presence of phosphorus atom
E_v	energy at upper edge of valence band	N_c	density of states in conduction band	w	precipitable water vapor in atmosphere (cm.)
f_c	ratio of radiative to non-radiative processes	N_v	density of states in valence band	W	space-charge region width, or solar cell width, in context
f_t	fraction of traps occupied by electrons	p	free hole density in extrinsic semiconductor material	α	carrier generation rate
f_{tp}	fraction of traps unoccupied by electrons	p_n	equilibrium hole concentration in n region	β	recombination rate constant
F	fill-factor	p_o	equilibrium hole concentration	Δ	net rate of energy loss
F_c	rate of radiative recombination	p_p	hole concentration in p region at equilibrium	ΔE	energy difference
F_{co}	rate of radiative recombination at equilibrium	p_l	hole density in valence band when $E_{fp} = E_t$	$\Delta E_1, \Delta E_2, \Delta E_3$	incremental photovoltages
F_s	carrier pair generation rate per unit area of cell exposed to sun	q	electronic charge	Δn	excess electron concentration
h	Planck's constant	Q	heat flux	Δp	excess hole concentration
I	current	Q_c	number of photons absorbed at cell surface per unit time per unit area	η_{max}	maximum efficiency
I_d	junction current under reverse bias	Q_s	carrier generation rate per unit area of cell exposed to sun	ν	frequency
I_L	light-generated current	R_s	series resistance	ν_g	photon frequency at absorption edge of material
I_m	maximum-power-point current	R_{sh}	shunt resistance	ϕ	integrated radiation flux
I_o	reverse saturation current	$R(0)$	rate of generation of hole-electron pairs by thermal processes	τ_i	excess carrier lifetime in intrinsic material
$I_{o(exp)}$	experimental reverse saturation current			τ_{no}	lifetime of electrons injected into p-type material
$I_{o(theor)}$	theoretical reverse saturation current			τ_o	minority carrier lifetime
I_{rg}	junction current arising from recombination and generation in the depletion region			τ_{po}	lifetime of holes injected into n-type material
I_{sc}	short-circuit current			ψ_D	built-in junction voltage

IV. CONTEMPORARY DEVELOPMENTS (1955-PRESENT)

A. THEORY

1. Junction Characteristics

The diffusion theory developed by Shockley explained the experimental facts with good accuracy for germanium diodes at room temperature. For wider bandgap semiconductors, however, the experimental results were found to differ from the theory in important ways. For silicon diodes, the I-V characteristic is generally found to be of the form

$$I = I_{o(\text{exp})} \left[\exp \left(\frac{qV}{AkT} \right) - 1 \right] \quad (58)$$

where $A > 1$, and $I_{o(\text{exp})} > I_{o(\text{theor})}$, $I_{o(\text{theor})}$ referring to the saturation current as determined from the diffusion theory. These two effects were later found to be generally related, diodes with large $I_{o(\text{exp})}$ values having larger A values, and conversely. The analysis of Sah, Noyce, and Shockley (183) proved an important advance toward resolving the problem expressed by Eq. (58) for many practical diodes.

The basis of this analysis was the inclusion of recombination and generation phenomena through a trapping level in the p-n junction space-charge region, which had been excluded in the earlier diffusion theory. The effects of direct (band-to-band or radiative) recombination and Auger-type (three-body) recombination were assumed small compared with the intermediate-level process.

The kinetics of the recombination mechanism, which were investigated and described earlier by Shockley and Read (184), formed the backbone of this analysis. The following discussion will attempt to explain the aspects of the Sah-Noyce-Shockley theory (183) as far as they are relevant to solar cell theory, that is, primarily in their application to a p-n junction under small forward bias. A schematic of the band structure under consideration is shown in Figure 29.

Four processes can occur: (i) An electron drops from the conduction band into the trap, to recombine with a trapped hole. (ii) A trapped electron is emitted into the conduction band. (iii) A trapped electron drops into a hole in the valence band and recombines. (iv) An electron is emitted into the trap from the valence band (a process equivalent to a trapped hole being emitted into the valence band).

For process (i)

$$\text{Trapping rate} = n f_{tp} / \tau_{no} \quad (59)$$

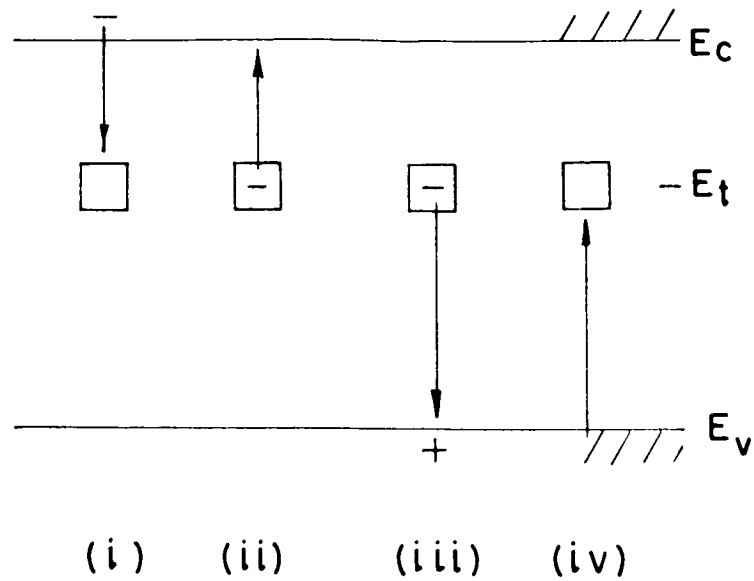


Figure 29. Energy band scheme for a semiconductor with trapping levels, after Sah et al.

where

n = density of electrons in the conduction band

f_{tp} = fraction of traps unoccupied by electrons

τ_{no} = lifetime of electrons injected into p-type material

Now:

$$n = n_i \exp \left(\frac{E_{fn} - E_{fi}}{kT} \right) \quad (60)$$

where

n_i = intrinsic electron density

E_{fn} = quasi-Fermi energy giving the distribution of electrons in the conduction band

E_{fi} = intrinsic Fermi energy

It is useful to define an electron density:

$$n_1 = n_i \exp \left(\frac{E_t - E_{fi}}{kT} \right) \quad (61)$$

where

n_1 = density of electrons in conduction band when $E_{fn} = E_t$

E_t = trap energy (see Figure 29)

Combining Eqs. (60) and (61):

$$n = n_1 \exp \left(\frac{E_{fn} - E_t}{kT} \right) \quad (62)$$

If

$$f_t = \text{fraction of traps occupied by electrons} = 1 - f_{tp} \quad (63)$$

then the rate of electron emission can be written as

$$\text{Emission rate} = a f_t \quad (64)$$

where a is a rate constant.

By Fermi-Dirac statistics

$$f_t = \frac{1}{1 + \exp \left(\frac{E_t - E_{ft}}{kT} \right)} \quad (65)$$

where E_{ft} = quasi-Fermi energy giving occupancy probability for trap level E_t .

In thermal equilibrium, $E_{ft} = E_{fn}$ and the trapping and emission rates must be equal. Under this condition, combining Eqs. (59) and (62-65):

$$a = \frac{n}{\tau_{no}} \cdot \frac{f_{tp}}{f_t} = \frac{n_1}{\tau_{no}} \quad (66)$$

Under nonequilibrium conditions (e.g., electrons injected into p-type material), the electron trapping rate will exceed the emission rate, and the net loss rate of electrons will be

$$U_{cn} = \frac{(n f_{tp} - n_1 f_t)}{\tau_{no}} \quad (67)$$

Similarly, for holes

$$U_{cp} = \frac{(p f_t - p_1 f_{tp})}{\tau_{po}} \quad (68)$$

where

p = density of holes in valence band

p_1 = density of holes in valence band when the Fermi level is at E_t (thermal equilibrium conditions)

Under nonequilibrium but steady-state conditions,

$$U_{cn} = U_{cp} = U \text{ (say)}$$

Substituting $f_{tp} = 1 - f_t$ and solving Eqs. (67) and (68) simultaneously gives

$$f_t = \left(\frac{n}{\tau_{no}} + \frac{p_1}{\tau_{po}} \right) \bigg/ \left[\frac{(n + n_1)}{\tau_{no}} + \frac{(p + p_1)}{\tau_{po}} \right] \quad (69)$$

and this can be substituted into Eq. (67) or (68) which gives, because of the thermal equilibrium condition $n_1 p_1 = n_i^2$

$$U = (pn - n_i^2) \bigg/ \left[(n + n_1) \tau_{po} + (p + p_1) \tau_{no} \right] \quad (70)$$

This expression was then applied to a p-n junction with simplified parameters, to demonstrate qualitatively the effect of recombination-generation current on the I-V characteristic. The band structures of the three regions of the device under consideration are shown in Figure 30. To simplify the analysis, it is assumed that the trapping level is at the intrinsic Fermi level energy in all regions of the device, so that $n_1 = p_1 = n_i$.

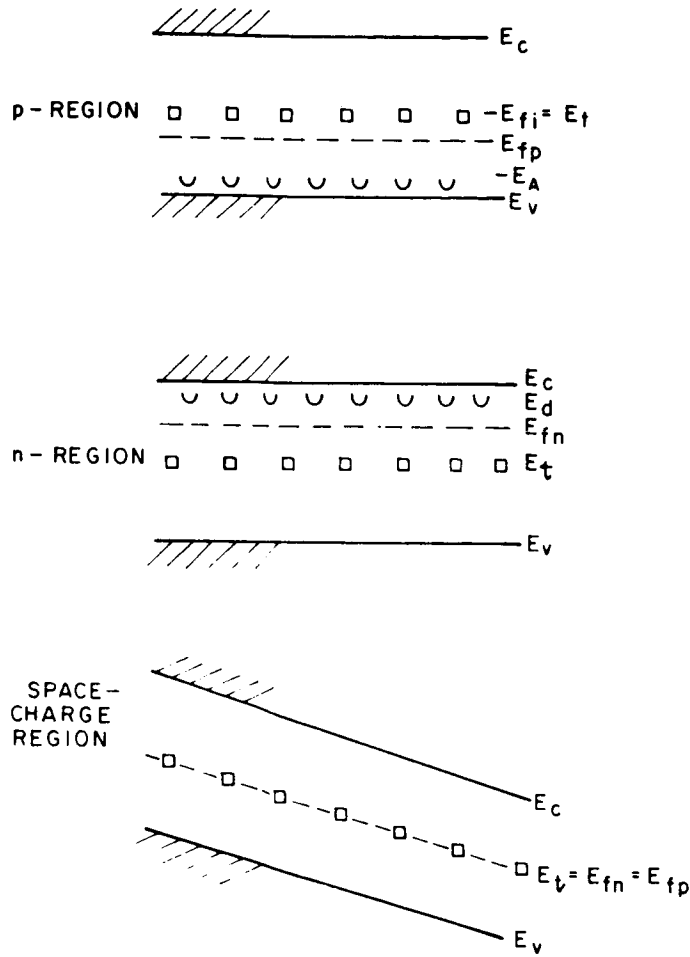


Figure 30. Band structures in the three regions of a p-n junction with trapping levels, after Sah et al.

It is also assumed for simplicity that the minority-carrier densities, lifetimes, and mobilities are the same in the p- and n-type regions. In a region which is appreciably p-type, the acceptor concentration must considerably exceed the trap concentration, and, hence, the equilibrium Fermi level must lie below E_t . Thus, in equilibrium most of the traps are vacant, ready to accept electrons which are injected. Writing

p_p = hole concentration in p-region at equilibrium

n_p = electron concentration in p-region at equilibrium

Then, if an excess concentration Δn of electrons arises by injection into the p-region

$$n = n_p + \Delta n \quad (71)$$

To maintain charge neutrality

$$p = p_p + \Delta n \quad (72)$$

The condition for "small injection" is that the hole concentration is not appreciably altered by the injection process.

Hence,

$$p_p \gg \Delta n \quad (73)$$

and the following conditions apply

$$p = p_p \gg p_1 = n_1 \quad (74)$$

Substituting into Eq. (70) and neglecting small quantities as indicated by the inequalities above,

$$U = \Delta n / \tau_{no} = (n - n_p) / \tau_{no} \quad (75)$$

Similarly, for the n-region

$$U = \Delta p / \tau_{po} = (p - p_n) / \tau_{po} \quad (76)$$

Now for n- and p-regions adjacent to the space-charge region in a reverse-biased junction, minority carriers generated in these regions will diffuse into the space-charge region, where they will slide rapidly down the potential gradient and be lost to the region of opposite conductivity type. Hence, in a p-type region adjacent to the space-charge region, n will be small, and Eq. (75) becomes

$$U = -n_p / \tau_{no} \quad (77)$$

Similarly, in an n-type region adjacent to the space-charge region

$$U = -p_n / \tau_{po} \quad (78)$$

The negative signs of the recombination rates indicate that a net generation process is occurring, as would be expected from the physics of the situation.

On the average, all minority carriers (both holes from the n-side and electrons from the p-side) generated within one diffusion length of the edge of the space-charge region will

cross the junction, thus giving rise to a total external current under reverse applied bias voltage of

$$I_d = -2q n_p L_o / \tau_o \quad (79)$$

per unit area of junction,

where

$$n_p = p_n$$

$$L_o = \text{minority-carrier diffusion length on both sides of the junction}$$

$$\tau_o = \tau_{no} = \tau_{po}$$

This diffusion current contribution is that contained in Shockley's earlier theory.

In the space-charge region of the device under reverse bias, as shown in Figure 30, carriers in both the conduction and valence bands are rapidly removed from the region by the field. Hence, recombination processes can be neglected in the space-charge region.

Therefore,

$$n_i \gg n = p \quad (80)$$

and

$$U = -n_i / 2 \tau_o \quad (81)$$

This gives rise to an external current

$$I_{rg} = -q W n_i / 2 \tau_o \quad (82)$$

per unit area of junction, where W = space-charge region width.

The ratio of the current generated in the space-charge region to that generated by the diffusion processes is then

$$\frac{I_{rg}}{I_d} = \frac{W n_i}{4 n_p L_o} \quad (83)$$

Putting $n_p = p_n = n_i^2/n_n$

$$\frac{I_{rg}}{I_d} = \frac{W n_n}{4 n_i L_o} \quad (84)$$

For a material such as germanium where n_i is large at or above room temperature, this ratio is typically 0.1. For silicon, however, the ratio can be 10^3 or higher, which means that the current generated in the space-charge region dominates over that due to diffusion. Under reverse bias, where the space-charge region widens, the reverse saturation current will not saturate, but will increase with $V^{1/3}$ for linearly graded junctions, and $V^{1/2}$ for abrupt junctions.

This effect will be even more pronounced in semiconductors with short minority-carrier lifetimes (leading to small L_o) and with large bandgaps, resulting in still lower n_i values.

Sah et al. pointed out that if generation in the space-charge region dominates the reverse-bias characteristic, recombination in the same region can be expected to have a large effect on the forward-bias characteristic. Under conditions of small forward bias, the band structure of the device is as shown in Figure 31, as discussed in Shockley's original paper on p-n junction characteristics. At the center of the p-n junction [$x = 0$ in Figure 31], the carrier concentrations are determined by the deviation of the quasi-Fermi levels by $V/2$ from the Fermi level, which at this point is equal to E_{fi}

$$p = n = n_i \exp\left(\frac{qV}{2kT}\right) \quad (85)$$

The recombination rate at this point is then

$$U = \frac{n_i \exp(qV/2kT)}{2\tau_o} \quad (86)$$

Because the minority-carrier concentrations on each side of this center point fall off with distance, the excess carrier concentration falls off exponentially with a characteristic length of kT/qE where E is the electric field in the junction. Thus, the recombination current density is

$$I_{rg} = \frac{(kT/qE)qn_i}{\tau_o} \exp\left(\frac{qV}{2kT}\right) \quad (87)$$

If a linear potential gradient across the junction is assumed, then $E = (\psi_D - V)/W$, where ψ_D is built-in voltage of junction.

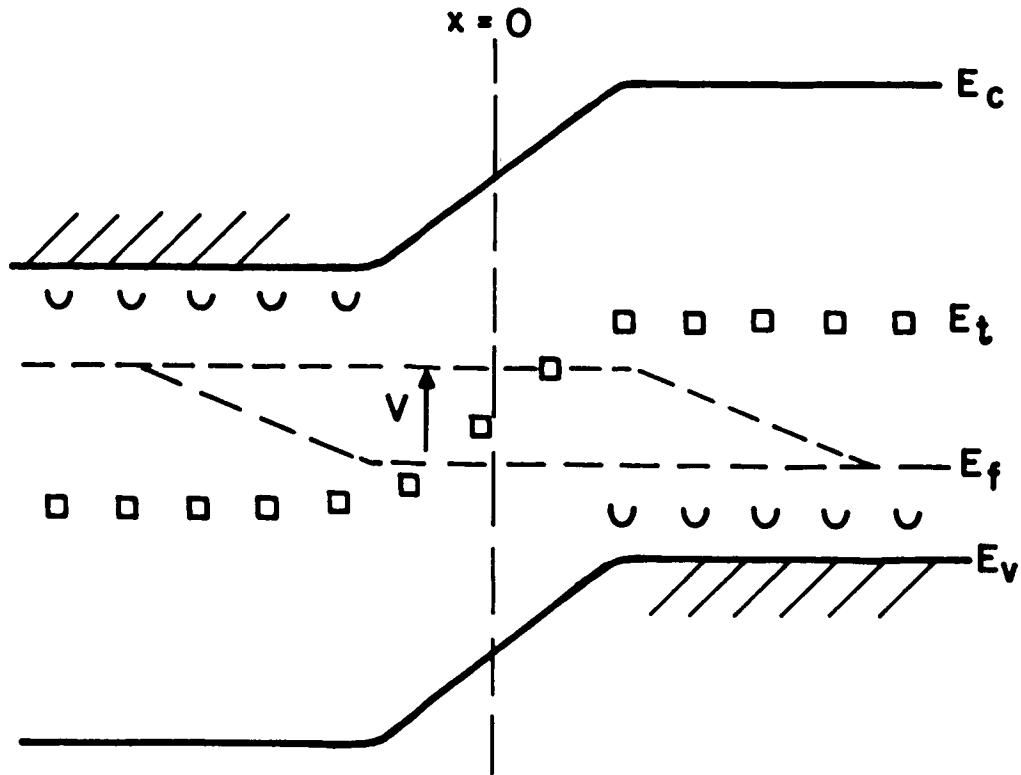


Figure 31. Band structure of a p-n junction under small forward bias

As shown by Shockley's original analysis, the diffusion current is given by

$$I_d = \frac{2qn_p L_o}{\tau_o} \exp \left(\frac{qV}{kT} \right) \quad (88)$$

The ratio of recombination current to diffusion current is

$$\frac{I_{rg}}{I_d} = \left(\frac{n_n}{n_i} \right) \left(\frac{W}{2L_o} \right) \left[\frac{kT}{q(\psi_D - V)} \right] \exp \left(\frac{-qV}{2kT} \right) \quad (89)$$

Again, for junctions in germanium this ratio is normally small, but for junctions in silicon it can be greater than 1, at low voltages. This theory predicts values of A in Eq. (58) as high as 2, for the cases where recombination inside the space-charge region dominates the forward current. Sah, Noyce and Shockley then proceeded to investigate a more general case, where the trapping level is located at an energy other than the intrinsic Fermi level. Using Fermi-Dirac statistics, the various carrier concentrations were determined from the energy levels present, and these were substituted into Eq. (86) to obtain the recombination rate. This rate was then integrated over the space-charge region to obtain the recombination-generation current arising in this region. To do this accurately, a linear variation of electrostatic potential could no longer be assumed (as

done in the previously discussed case), and the quasi-Fermi levels for holes and electrons had to be known as functions of distance in the junction region. Numerical methods had to be used to obtain a solution, and it would be inappropriate to devote the necessary space to present details here.

The major conclusions were:

In the region of large reverse bias, the current does not saturate as found in earlier p-n junction theories, but follows a $V^{1/3}$ law for linearly graded junctions and a $V^{1/2}$ law for abrupt junctions.

Under small forward bias, the recombination current density is given by

$$I_{rg} = \frac{q n_i}{(\tau_{po} \tau_{no})^2} W \frac{2 \sinh(qV/2kT)}{[(\psi_D - V)q/kT]} \times f(b) \quad (90)$$

where

$$f(b) = \int_{\delta_1}^{\delta_2} \frac{d\delta}{\delta^2 + 2b\delta + 1} \quad (91)$$

with

$$b = \exp\left(\frac{-qV}{2kT}\right) \cosh \left[\frac{E_t - E_i}{kT} + \frac{1}{2} \ln \left(\frac{\tau_{po}}{\tau_{no}} \right) \right] \quad (92)$$

and

$$\delta_{1,2} = \left(\frac{\tau_{po}}{\tau_{no}} \right)^{1/2} \exp \left[\pm \frac{(\psi_D - V)q}{2kT} \right] \quad (93)$$

Analysis of this expression for I_{rg} showed that the value of A in Eq. (58) will vary with the value of applied bias V and will have a maximum value of about 1.75.

The remainder of Sah, Noyce and Shockley's paper was devoted to analysis of transistor characteristics, and is of no application to photo-voltaic devices. This account of the theory has been given in detail because this represents the present status of rigorous analytical examination of diode characteristics theory. In practice, A values considerably larger than those which can be accounted for under this theory are observed. Various

explanations have been offered for this phenomenon, but as far as can be determined, none of these have been analyzed in sufficient detail to allow comparison between theory and experiment to unambiguously determine the validity or otherwise of the proposals. These matters are further discussed in the section of this report in which theoretical research is evaluated.

2. Ultimate Conversion Efficiencies

As described above, a calculation of maximum theoretical efficiency was first performed by Cummrow, whose results were extended by Rittner. These results were published on the eve of the announcement of the Bell solar battery, the first practical silicon cell. Following this event, Prince (145) published an account of the device, which included a calculation of the theoretical efficiency of silicon cells operated under earth-surface illumination. Prince's calculation followed these steps:

- (i) The short-circuit current I_{SC} was calculated by assuming a unity collection efficiency and using that portion of the photon flux of earth-surface sunlight (from an early spectral distribution) for which the photon energies exceed the bandgap of the semiconductor used, since this determines the minimum energy required to create hole-electron pairs by photon absorption. He obtained a value for I_{SC} in silicon of $44 \text{ mA} \cdot \text{cm}^{-2}$, which he reduced to a "likely maximum" of $35 \text{ mA} \cdot \text{cm}^{-2}$ to allow for optical reflection losses.
- (ii) I_0 was calculated from Shockley's diffusion analysis of p-n junction behavior, for a junction formed between a heavily doped p-region and a moderately doped n-region, using measured values of material constants such as carrier mobility and lifetime.
- (iii) From the I-V characteristic according to diffusion junction theory, including results of (i) and (ii) above, the maximum power available was calculated.

After performing these calculations for a variety of bandgaps, Prince was able to plot theoretical efficiency as a function of semiconductor energy gap. These calculations were, however, based on empirical semiconductor data obtained for silicon, which were assumed to apply also for materials with different bandgaps.

Further work in this area has been supported in part by research contracts by government agencies; for a summary of the chronology of these, the reader is referred to Table XVI in Appendix III.

Loferski (185), working under a Singal Corps contract (152) aimed at investigating materials for photovoltaic power conversion devices, refined the previous analysis. This work used the solar spectral distributions for various atmospheric conditions and elevation angles, in their dependence on meteorological factors which alter the

sunlight spectral content as well as that outside the atmosphere. For the ultimate-efficiency calculations, optical reflection and collection-efficiency effects were assumed not to contribute losses, and the saturation current I_0 for the junction was calculated from the junction diffusion-theory analysis, using measured values for semiconductor conduction parameters. The analysis was thus, in principle, similar to those done before, but with more accurate sunlight spectra used, providing families of curves showing conversion efficiency as a function of energy gap, for various air-mass, water-absorption, and cloud conditions. Further, Loferski considered the effect of the departures of I_0 from the values predicted by the diffusion theory, giving further families of efficiency/bandgap curves for values of I_0 increased by various constant factors, as well as for $I_0 \propto \exp(-E_g/2kT)$ instead of the normal $I_0 \propto \exp(-E_g/kT)$. These results showed that the effects of these departures from theory for I_0 was to shift the bandgap of the optimum material to higher values for the increased saturation currents, and to lower values for the $I_0 \propto \exp(-E_g/2kT)$ case.

Loferski also investigated the dependence of collection efficiency on junction depth, minority-carrier diffusion length, optical absorption constant, and surface recombination velocity, considering, however, collection from the diffused surface region only.

Vavilov's paper (186), in 1956, appears to be the first mention of efficiency analyses by Soviet workers. This analysis is a review of the work published by Pfann and van Roosbroeck and by Rittner, and adds nothing to their results. Similarly, the efficiency analysis work of Loferski and other Western authors is heavily drawn upon in a Soviet book containing sections on photovoltaic conversion (187) published in 1958; no new results (on such analyses) are quoted in this work.

The question of the effect of temperature on the optimum E_g value for solar energy conversion was taken up by Halsted of the GE Research Laboratory. Results of his analysis were reported briefly in 1957 (188), in which an analysis based on the methods of Prince (145) was used to plot solar conversion efficiency (theoretical maximum) as a function of E_g for temperatures between 300 and 600 °K. The results showed that the optimum E_g shifts to higher values with increasing temperature, since the loss in I_{SC} with increasing E_g is more than compensated by the decrease in I_0 theoretically predicted. Although the predicted effects on I_0 are not those seen in practice, experimental work has shown that GaAs, with a larger bandgap than that of silicon can give higher efficiencies at temperatures above 150°C, even though the silicon cells are more efficient at room temperature.

The same question was taken up in great detail by Rappaport and Wysocki (189, 190), during work supported by the U.S. Army Signal Corps Research and Development Laboratory (191), a continuation of the contract which supported Loferski's analysis. The analytical approach was essentially that of Loferski, but three types of behavior governing I_0 were considered: (i) I_0 obeying the diffusion theory of Shockley, (ii) I_0 having contributions from both diffusion theory and recombination effects as discussed by Sah,

Noyce, and Shockley (an account is given in IV-A-1), and (iii) I_0 due wholly to recombination current. The analysis for these three cases then proceeded according to Loferski's methods, but with measured (or estimated) values for semiconductor parameters such as mobility, lifetime, and effective masses, and intrinsic carrier densities for the materials Ge, Si, InP, GaAs, CdTe, AlSb, $\text{GaAs}_{0.7}\text{-P}_{0.3}$, $\text{GaAs}_{0.5}\text{-P}_{0.5}$, and CdS. This should be contrasted with the usual assumption of semiconductor parameters being equal to those of silicon in the analyses of Prince and Wolf. Thus, the results obtained in this analysis reflect strongly the state of materials technology at the time the work was done. Even so, the results follow very much the form expected from Loferski's work, and the main conclusion is that GaAs should be superior to silicon for high-temperature use, a prediction borne out by practice, as mentioned above.

This paper was valuable in providing a large number of curves showing the effect of temperature and the various values of I_0 on the efficiency.

A logical extension of this type of analysis was given by Wolf and Prince (192, 193), with a more complete account having been given later by Wolf (194). Since this work is probably the most comprehensive of its type, a fairly full discussion will be given, to compare and contrast with the thermodynamic analysis given later. The cell considered is a planar p-on-n cell operating under direct sunlight, using the same spectral distribution as used previously by Prince. The analysis proceeded by the following steps:

- (i) Reflection from the front surface of the cell need be only briefly considered, since it had been reduced to very low values (about 3%) by the mysterious black surface layer obtained from the boron trichloride diffusion process, or could otherwise be reduced to similar values by conventional optical coating techniques.
- (ii) The effect of spectral dependence of optical absorption coefficient has two principal results. First only photons with energy greater than that required to create hole-electron pairs (i.e., $> E_g$) are absorbed in the cell (neglecting relatively minute free carrier absorption), and thus the portion of the sunlight spectrum which is usable for conversion in the cell is dependent on the bandgap of the semiconductor. Secondly, because the optical absorption coefficient in the hole-electron pair creation region is finite, then in a cell of finite thickness, some photons potentially able to create hole-electron pairs will pass through the cell without being absorbed and will thus be lost. This effect is predominantly found at wavelengths close to the absorption edge, where the absorption coefficient is smaller. An expression showing the effects of these two processes was derived using Lambert's law of optical absorption, and involving the cell thickness and the variation of optical absorption coefficient with wavelength.

(iii) Photons having more energy than the minimum needed for hole-electron pair creation impart all of their energy to the free carriers on absorption, but very rapid processes cause the free carriers to lose energy by generating phonons (heat) until they are at the energy corresponding to the band edge valance band edge (E_v) for holes, conduction band edge (E_c) for electrons. Thereafter, the only energy available for useful work in the cell corresponds to the energy separation of the hole-electron pairs, $E_c - E_v = E_g$. Because of (ii) and (iii), semiconductors with small E_g can absorb large numbers of photons, but each photon absorbed can potentially do only a small amount of useful work corresponding to E_g . Conversely, semiconductors with larger bandgaps (E_g) absorb a smaller number of photons, but each photon can potentially do a larger amount of work. Arising from the interaction of these two competing processes, a plot of usable energy as a function of E_g for illumination with the spectrum of sunlight shows that a maximum of 46% of the photon energy is potentially available to do useful work, and that this 46% occurs for $E_g = 0.9$ eV.

(iv) Hole-electron pairs are generated in the volume of the cell, but to contribute to power output, the minority carriers must diffuse to the junction plane of the cell. Because of the finite diffusion length for minority carriers, this collection process is not 100% efficient. Wolf and Prince set up and explicitly solved differential equations describing this process, including both the p- and n-regions of the cell, Lamberts optical absorption law being used to give the spatial dependence of carrier generation, and surface recombination in both regions being accounted for, through the boundary conditions. Thus, the carrier distributions as a function of distance from the front surface of the cell were derived. From these, expressions were derived for the output current contributions from the n- and p-regions as a function of wavelength of illumination. From these expressions the collection efficiencies as a function of wavelength, separately for the n- and p-regions, were plotted for a silicon cell with measured semiconductor parameters. These were added to give the total collection efficiency, from which the spectral response of the cell can be derived. A comparison between calculated and measured values for this function was given in (193).

(v) Although in principle the open-circuit voltage V_{oc} of a cell may reach E_g/q in the limiting case, $V_{oc} < E_g/q$ in practice, and the actual value of V_{oc} was calculated by Wolf and Prince using Shockley's diffusion theory for junction behavior, the calculation being essentially identical with that given by Loferski, as described above. As has already been pointed out, such a calculation relies on obtaining a value for the reverse saturation current (I_0) from empirical semiconductor parameters. Using Shockley's expressions, Wolf and Prince calculated a curve showing V_{oc}/E_g as a function of energy gap E_g , it being assumed that semiconductor parameters such as minority-carrier lifetime and mobility are the same as those measured in silicon; i.e., variations

in I_0 occur only by changes in E_g . This is a most important assumption, which has been made in all calculations of this type by other workers. On this assumption rest all calculations showing that increasing E_g increases V_{oc} ; the validity of this result will be examined in the evaluation of cell theory later in this report.

- (vi) Because of the exponential nature of the theoretical cell I-V characteristic, the actual cell voltage at the maximum power working point (V_m) is less than V_{oc} , and for similar reasons, the maximum power point current I_m is less than the short-circuit current I_{sc} , both by amounts which can be calculated from the cell characteristic. Wolf and Prince calculated a "curve factor" = $(V_m \times I_m) / (V_{oc} \times I_{sc})$ from the cell characteristic, again using Shockley's diffusion theory for the cell I-V curve.
- (vii) Resistive elements in the cell equivalent circuit cause loss of power, but the effects of shunt resistance R_{sh} in parallel with the cell junction may be neglected in commercial silicon cells. However, series resistance R_s must be considered, especially since the analysis of (iv) showed that the diffused surface region should be as thin as possible to maximize collection efficiency, but also, that this tends to increase the contribution of the surface-layer resistance to the R_s of the cell.

Combining the effects (i) through (vii) an expression for overall conversion efficiency can be derived. In the "ideal cell", where surface reflection is zero, all photons with energy $\geq E_g$ are absorbed and produce one hole-electron pair each, where all such pairs contribute to cell output (i.e., unity collection efficiency), and where $R_s = 0$, a maximum efficiency may be calculated, which is a function of E_g because of the effects described in (ii), (iii), (v) and (vi). Wolf and Prince showed a curve for η_{max} as a function of E_g , indicating $\eta_{max} = 23.6\%$ for $E_g \approx 1.3\text{eV}$, the curve having a rather broad maximum and being in good agreement with the results of Loferski. Wolf (193) then goes on to discuss various schemes for improving the conversion efficiencies; these are discussed later together with proposals by others.

In this section we have seen how successively more comprehensive analyses of ultimate theoretical efficiency were derived for devices made with p-n junctions which were assumed to operate with characteristics described by Shockley's diffusion theory. Because these analyses all require values for semiconductor parameters such as lifetime, mobility, and surface recombination velocity, to give numerical results, they depend on empirical data.

This "practical" type of analysis is to be contrasted with other "theoretical" analyses which have been derived from thermodynamical arguments, and which are based on fundamental physical constants to provide numerical estimates of ultimate device conversion efficiency.

The first analysis of this type was performed by Müser, whose results were published in 1957¹⁰ (195). Müser considered an energy conversion system operating as shown schematically in Figure 32. The sun is considered to be a black-body at temperature T_1 , which produces an energy flux N_{12} into the cell. This energy causes hole-electron pair creation in the semiconductor, and the resulting carrier densities can be characterized by a temperature T_2 . Energy is lost from the carriers by three processes:

- (i) Radiative hole-electron recombination, whereby photons are re-emitted from the semiconductor (N_{21} in Figure 32).
- (ii) Nonradiative hole-electron recombination, which gives up heat to the semiconductor lattice (N_{23} in Figure 32).
- (iii) Hole-electron recombinations which potentially are available to do useful work (N_{2M} in Figure 32).

Now the most efficient conversion of recombination energy into useful work will occur when M is a Carnot engine, and the useful energy output N is then given by

$$N = (N_{12} - N_{21} - N_{23}) \times \left(\frac{T_2 - T_3}{T_2} \right) \quad (94)$$

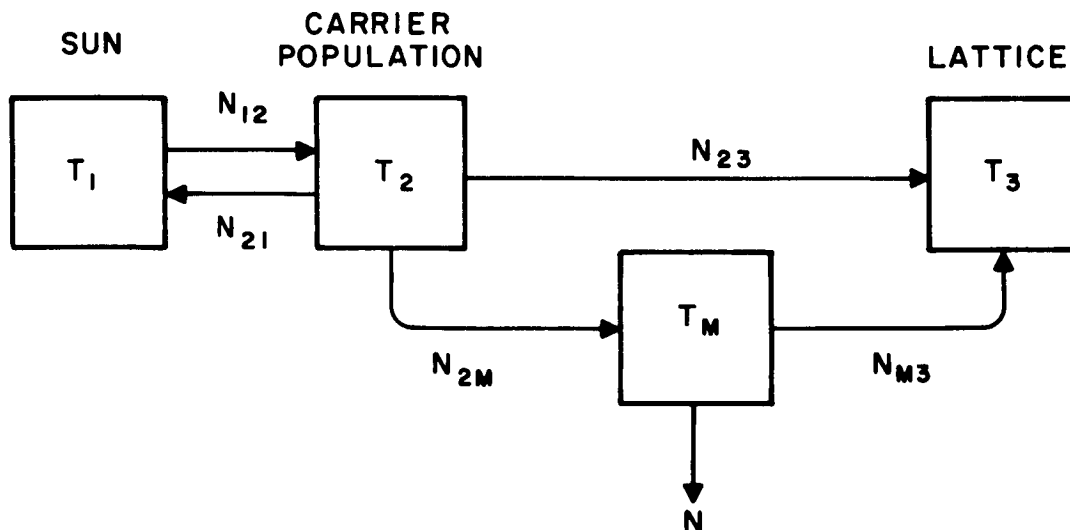


Figure 32. Energy conversion system, after Müser

¹⁰Müser's treatment is based on thermoelectric arguments which make the analysis of general application to several different devices, but which are somewhat cumbersome for use with specifically photovoltaic devices. Hence, the account given here differs in detail from that of Müser, but the basic arguments are identical.

Efficiency $\eta = N/N_{12}$; N_{12} is fixed, and hence η is maximized when N is maximized. Considering T_3 as fixed, N may be maximized by adjusting T_2 , remembering that $(N_{21} + N_{23})$ is also a function of T_2 .

Forming dN/dT_2 from Eq. (94) and equating to zero, it can be shown that

$$\frac{d(N_{21} + N_{23})}{dT_2} = (N_{12} - N_{21} - N_{23}) \times \frac{T_3}{T_2 (T_2 - T_3)} \quad (95)$$

This specifies the temperature T_2 at which maximum conversion efficiency is obtained, and is derived from purely thermodynamic premises. To apply this to a photovoltaic converter, it is necessary to know how $(N_{21} + N_{23})$ varies with T_2 . Müser then points out that in a semiconductor under illumination, the electron and hole densities (n and p) can be characterized by a temperature T_2 such that

$$pn = N_c N_v \exp \left[\frac{-E_g}{kT_2} \right] \quad (96)$$

where N_c , N_v are the density of states in the conduction and valence bands, respectively

E_g is the forbidden bandgap
 k is Boltzmann's constant

In the equilibrium case, for intrinsic material

$$p_o n_o = N_c N_v \exp \left(\frac{-E_g}{kT_3} \right) = n_i^2 \quad (97)$$

where T_3 is the equilibrium temperature and $p_o = n_o = n_i$.

If the only recombination mechanism is a direct hole-electron annihilation, then recombination can be described by the expression

$$\frac{dn}{dt} = \alpha - \beta pn \quad (98)$$

where

$\frac{dn}{dt}$ is the rate of change of electron density

α is the generation rate (which must include both thermal and photon-induced generation)

β is the recombination constant

In equilibrium, $dn/dt = 0$, and hence from Eq. (98)

$$p_o n_o = n_i^2 = \alpha/\beta \quad (99)$$

Also from Eq. (96) it can be shown that the recombination is exponential, with a rate for intrinsic material

$$\tau_i = \frac{1}{2\sqrt{\alpha\beta}} \quad (100)$$

Combining Eqs. (96), (97), (99) and (100) it can be shown that:

$$\beta (pn - p_o n_o) = \frac{n_i}{2\tau_i} \left\{ \exp \left[\frac{E_g}{k} \left(\frac{1}{T_3} - \frac{1}{T_2} \right) \right] - 1 \right\} \quad (101)$$

Since each electron-hole recombination causes energy E_g to be either radiated from the cell (for a radiative transition), or given up to the lattice (as thermal energy), then the rate of loss of energy from the excited electron distribution is $(\beta pn E_g)$ per unit volume. However, thermal excitation processes continually supply energy to the electron distribution, at a rate $(\beta p_o n_o E_g)$ per unit volume. Hence, the net rate of loss of energy per unit volume from an electron distribution is

$$\Delta = E_g \times \beta (pn - p_o n_o) = \frac{n_i E_g}{2\tau_i} \left\{ \exp \left[\frac{E_g}{k} \left(\frac{1}{T_3} - \frac{1}{T_2} \right) \right] - 1 \right\} \quad (102)$$

Thus $\Delta = N_{21} + N_{23}$ in Eq. (95), and by combining Eqs. (95) and (102), the (T_2) for maximum efficiency can be obtained. Then noting that in Figure 32

$$N_{2M} = N_{12} - (N_{21} + N_{23}) \quad (103)$$

N , and hence the efficiency, can be determined. These equations can only be solved by numerical methods, and aside from noting that he used $\tau_i = 10^{-4}$ sec, Müser gives none of the values of the parameters used in his solutions, so that it is difficult to check on his calculations for this stage of the analysis. It should be noted that N_{12} is the energy imparted to the carrier population by the incident illumination and does not include the energy in the photons which do not create hole-electron pairs, nor the excess energy ($>E_g$) imparted to hole-electrons pairs by photons of energy greater than E_g . The value of N_{12} is obtained by an integration similar to that of Wolf (described above), in which it is shown that a maximum of 46% of the black-body radiation is available to create the carrier population under illumination. Müser shows in a family of curves how (N/N_{12}) depends on illumination intensity and E_g , and he states that the maximum theoretical

efficiency for a silicon cell is 16%. This value is too low, for reasons which are not easy to ascertain since so little of the calculation is shown. However, a contributory factor is the τ_i value of 10^{-4} sec, which is much smaller than that implied by Shockley in a later analysis.

Rose (196) developed a thermodynamic analysis for the efficiency of the photovoltaic conversion process in 1960. Where Müser had ascribed a temperature to the carrier population in the devices, Rose developed an expression by which the effective temperature of the incoming photon stream was characterized. This was used to derive an expression for the maximum voltage which could be developed by a photovoltaic device, rather than deriving the conversion efficiency. Briefly, the derivation ran as follows.

If the device is illuminated uniformly from all directions by a light flux, then the flux can be described by a dimensionless number $L(\nu)$ which is the ratio of the incident flux of frequency ν , per unit area and unit ν , to the radiation which would be emitted by a black-body at the operating temperature of the device, at the same ν . Then

$$L(\nu) = \frac{f(T_2, \nu)}{f(T_1, \nu)} \quad (104)$$

where

$$f(T, \nu) = \frac{\text{const}}{\exp\left(\frac{h\nu}{kT}\right) - 1} \quad (105)$$

and $\text{const} = 2\pi\nu^2/C^2$ which cancels in the ratio. Equation (104) defines a temperature T_1 which is characteristic of the incident radiation. For the case of nonuniform illumination, e.g., the sun in a 'cold' sky with no concentration, a geometrical factor will enter into the calculation of $L(\nu)$, but the analysis remains the same in principle. The best conversion efficiency will be achieved if a Carnot engine operates with a source temperature T_1 and a sink temperature T_2 for the conversion process, so that the maximum power output per unit area is given by

$$P = Q \frac{T_2 - T_1}{T_2} = [L(\nu) - 1] f(T_1) L\nu \left(\frac{T_2 - T_1}{T_2} \right) \delta\nu \quad (106)$$

where

Q = net heat flux per second

$\delta\nu$ = the frequency range of the incident illumination

and $f(T)$ is a function relating the number of photons of frequency ν emitted per unit area and time by a black-body to its temperature T . Thus, the net photon flux onto the device, per unit area, is

$$N = (L(\nu) - 1) f(T_1) \delta \nu \quad (107)$$

For a device working at unity quantum efficiency, the output current $I = N \times q$, and for $P = I \times V$, Eqs. (106) and (107) can be combined to yield

$$qV = L\nu \left(\frac{T_2 - T_1}{T_2} \right) \quad (108)$$

Substituting for T_2 from Eqs. (104) and (105), one obtains

$$V = \frac{h\nu}{q} \left\{ 1 - \frac{kT_1}{h\nu} \left[\ln \left(\exp \left(\frac{h\nu}{kT_1} \right) - 1 + L(\nu) \right) - \ln L(\nu) \right] \right\} \quad (109)$$

[In general, Eq. (106) must be integrated over the frequency range, if this is wide enough to cause appreciable changes in $L(\nu)$.] Rose then goes on to show that for the high illumination level and low illumination level cases, the usual logarithmic and linear dependences of V on illumination level are obtained from Eq. (109). Also, a plot comparing theoretical and experimental dependence of (V) on (L) for a germanium photovoltaic cell is given, demonstrating the departure from ideal performance, particularly at low light levels. Clearly, integration of Eq. (106) over the sunlight spectrum, with insertion of a suitable geometrical factor into Eq. (104), would yield an expression for the theoretical conversion efficiency of a photovoltaic energy converter. Although this was not done by Rose, an account of the derivation above has been given here because the ideas developed in it form part of the basis for the analysis of Shockley below.

A theoretical analysis of the maximum conversion efficiency for a photovoltaic device was performed by Shockley and Queisser, under contract with the USAF Aeronautical Systems Command (197): the analysis was also published in 1960 (198) and 1961 (199).

Believing that the analyses of the type described above were of limited use because of the need for empirical data on semiconductor properties to obtain conversion efficiency values, Shockley and Queisser derived an expression for cell efficiency from purely thermodynamic reasoning. The analysis proceeded by the following steps:

- (i) The Sun is taken as a 6000 °K black-body, and it is assumed that each photon of energy $\geq E_g$ creates one hole-electron pair from which E_g of energy is available. The integration process of earlier analyses (e.g., Wolf or Muser) is repeated, Shockley's results showing that 44% of the energy is potentially available (cf. 47% for Wolf's data from the measured solar spectral distribution, 46% for Muser's data for a 6000 °K black-body).

- (ii) The diode equation and its associated parameters are derived from purely thermodynamic reasoning: the derivation of a value for I_0 by this method is the kernel of the treatment.
- (iii) The maximum-power operating point, and the corresponding power, is derived by a curve-analysis method which is essentially conventional, as used by previous analyses (e.g., Loferski or Wolf).

Thus, the point at which Shockley departs from previous analyses is (ii) above, and only this portion of the analysis will be covered here.

Five generation and recombination processes were considered as occurring in a semiconductor to determine the rate of change of carrier concentration:

- (i) Photon-induced generation, caused by the incident illumination.
- (ii) The converse of (i), radiative hole-electron recombination.
- (iii) Thermal (nonradiative) carrier-generation processes.
- (iv) The converse of (iii), nonradiative recombination processes.
- (v) Removal of carrier pairs to another region of the device, where they do useful work (crossing the p-n junction in the cell provides this removal process).

Expressions for these were derived in turn:

- (i) If Q_s = carrier generation rate per unit area of cell exposed to the sun, then Q_s is calculated from the Planck distribution integrated to provide the number of photons of energy $h\nu \geq E_g$; i.e.,

$$Q_s = \frac{2\pi}{c} \int_{E_g/h}^{\infty} \frac{\nu^2 d\nu}{\exp\left(\frac{h\nu}{kT_s}\right) - 1} \quad (110)$$

where

- h = Planck's constant
- ν = frequency
- c = velocity of light
- T_s = temperature of the Sun (6000 °K)
- k = Boltzmann's constant

It is convenient to put

$$Q_s = Q(\nu_g, T_s) \quad (111)$$

Then if each photon with $h\nu \geq E_g$ creates one hole-electron pair, the rate of generation of carrier pairs per unit cell area is F_s where $F_s = Q_s$.

(ii) Consider a cell at a temperature T_c , completely surrounded by a black-body at the same temperature. Under this thermal-equilibrium condition, the rate at which photons with energy $h\nu \geq E_g$ are absorbed by the cell must equal the rate at which such photons are emitted by the cell by the radiative recombination process. For a cell under this equilibrium condition, Q_c photons with $h\nu \geq E_g$ are absorbed in unit time per unit area, where

$$Q_c = Q(\nu_g, T_c) \quad (112)$$

Under this condition,

$$F_{co} = 2 Q_c \quad (113)$$

where F_{co} = recombination rate for radiative processes: the factor 2 appears because the cell has two sides for both absorption and emission of radiation.

Now this recombination rate is proportional to the product of hole and electron concentrations, i.e.,

$$F_{co} = \text{const.} \times p_o n_o$$

where p_o, n_o , are the equilibrium hole and electron concentrations at equilibrium. Under illumination, these concentrations become p and n ,

$$F_c = F_{co} \frac{np}{n_o p_o} = F_{co} \exp \frac{V}{V_c} \quad (114)$$

where V is the difference in energy between the quasi-Fermi levels for holes and electrons (see Section IV-A-1), and $V_c = kT_c/q$. V is the voltage appearing at the cell terminals.

(iii) and (iv) are accounted for by putting

$R(O)$ = rate of generation of hole-electron pairs by thermal processes

$R(V)$ = rate of recombination of hole-electron pairs by nonradiative processes

One notes that when $V = 0$, these processes are equal and thus balance, as required.

(v) If the current provided by the cell is I , then the rate at which carriers are removed from the active region is $-I/q$.

In the steady-state condition, the rate of change of carrier concentration is zero, so that the above processes can be combined

$$F_s - F_c(V) + R(O) - R(V) + I/q = 0 \quad (115)$$

(One notes that the sign of I in Eq. (115) is negative when the cell is delivering power.) It is useful to introduce the quantity f_c , which is defined as the ratio of the numbers of radiative to nonradiative recombination-generation currents

$$f_c = \frac{F_{co} - F_c(V)}{F_{co} - F_c(V) + R(O) - R(V)} \quad (116)$$

In the particularly simple case where the nonradiative processes fit the ideal rectifier equation (as in germanium, but not silicon), one can put:

$$R(V) = R(O) \exp \frac{V}{V_c} \quad (117)$$

Under conditions where the cell is surrounded by a black-body at temperature T_c , the unilluminated thermal-equilibrium characteristic for the device can be obtained from Eq. (115) by substituting Eqs. (114) and (117), and noting that in this condition $F_s = F_{co}$; the result is

$$I = I_o \left(\exp \frac{V}{V_c} - 1 \right) \quad (118)$$

where

$$I_o = q [F_{co} + R(O)] \quad (119)$$

(The sign of I in this equation is the opposite of that in the original paper, to make it consistent with the remainder of this report.)

The value of I_o can thus be determined from Eq. (119) by noting that $Q_c = 1.7 \times 10^3 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ for $E_g = 1.09 \text{ eV}$ and $T_c = 300^\circ \text{K}$. If nonradiative transitions are neglected ($f_c = 1$), this leads to an I_o value of $5.4 \times 10^{-16} \text{ A}$ for a 1-cm^2 cell (i.e., $1 \text{ cm} \times 1 \text{ cm}$ cell, one surface of which is active, but both surfaces of which contribute to I_o).

Shockley then uses I_0 values derived as above to calculate maximum efficiency as a function of E_g . Further, by insertion of various values of f_c between 1 and 10^{-12} , a family of efficiency vs. E_g values are generated. Shockley shows that according to the above analysis, the maximum theoretical efficiency for a silicon solar cell operating under direct sunlight (i.e., without concentrators) is 30%. This is considerably higher than the results calculated by the methods above, and the reasons for this are discussed by Shockley. Some of the calculations are summarized in Table I.

TABLE I. RESULTS OF ULTIMATE THEORETICAL EFFICIENCY CALCULATIONS

Author	Illumination Source	Illumination Intensity (mW cm^{-2})	Optimum E_g (eV)	Efficiency Of Silicon Cell (%)
Cummerow	5760°K ⁽¹⁾	108	~ 2	17
Rittner	5760 °K ⁽¹⁾	100	1.50	22.5
Pfann + van Roosbroeck	Sunlight (see text)	86	not calculated	18
Prince	AM1 ⁽²⁾	108	1.38	21.7
Loferski	AM1 ⁽²⁾	106	1.43	20.5
Wolf	AM1 ⁽²⁾	100	1.26	21.6
Müser	6000 °K ⁽¹⁾	∞	not calculated	16
Shockley	6000 °K ⁽¹⁾	100	1.35	30
⁽¹⁾ Black-body ⁽²⁾ Air-Mass 1 sunlight ($m = 1$, $w = 2$)				

The differences in the results of the various theoretical treatments outlined above have an important bearing on solar cell research, and the reasons for the differences, and their significance, have been discussed by many authors.

As was pointed out by Loferski (200), numerical differences arise between essentially similar analyses if the spectral distributions used in the calculations differ. For this

reason, type and intensity of illumination must be specified in comparing divergent results, and this is just as important in theoretical as in experimental work. From the theoretical viewpoint, however, there are more fundamental differences between various analyses, and these we shall discuss here.

The basic divergence of all theories of solar cells stems from the value to be assigned to the reverse saturation current I_0 , and the factor A , in the diode equation

$$I = I_0 \left(\exp \frac{qV}{AkT} - 1 \right) \quad (120)$$

Workers have taken four discernible positions on these; in the ideal cell:

- (i) I_0 should be determined by wholly thermodynamic considerations, in which the only required recombinations are radiative, and $A = 1$.
- (ii) I_0 should be given by the diffusion theory, and A should be 1.
- (iii) I_0 should be given by recombination theory, and A may have values $1 \leq A \leq 2$.
- (iv) Experimentally determined values of I_0 and A should be used, since none of the above theories comes near to describing results seen in practice.

Clearly, (i) and (iv) represent extreme opinions, and most workers take a position sitting on one of the fences dividing the possible dogmas.

Shockley and Queisser have defended the position that the only fundamentally required recombination processes are radiative, and that nonradiative recombinations may be regarded as "imperfection effects", an exception being made for Auger-process recombination.¹¹ The possibility of Auger-processes modifying the I-V curve to produce the experimentally observed diode characteristic was very fully examined by P.T. Landsberg, working with Shockley and Queisser, the results being reported in Reference (201).¹²

¹¹In which energy and momentum are conserved in the recombination process by requiring that three carriers be involved. In the more usual nonradiative recombination processes, a large number of phonons must be produced to obtain this conservation.

¹²Note that in ASD-TDR-62-776, the text reference to Figure 19 on page 71 should be changed to Figure 18; also note that in the Figures, the graphs of 18 and 19 should be interchanged, but not the captions.

This work showed that although changes in the slope of the diode characteristic could be obtained if Auger processes were present, the changes are much too small to account for the experimental facts. Landsberg has also pointed out (202) that Auger effects probably become less significant as E_g increases. Since the major interest in solar cell theory is in materials with E_g greater than that for silicon, it appears that Auger effects probably do not play an important role in determining the efficiency of the cells.

As discussed in Section IV-A-1, Sah, Noyce, and Shockley showed that in the diode equation, A values between 1 and 2 could be accounted for by recombination-generation in the depletion region. Shockley and Henley (203) pointed out that if the recombination site density were position-dependent, and if the maximum-recombination plane in the depletion region moved to lower recombination-site densities under increasing forward bias, then values of $A > 2$ could result. This mechanism was analyzed in detail by Shockley and Queisser, under their USAF-funded study contract (201), and it was shown that if physically reasonable values were assumed for (i) the rate of change of recombination-site density with distance, and (ii) the ratio of hole-to-electron interaction cross sections for the recombination center, then this mechanism could not account for the experimentally observed values of A .

Wolf (194) has pointed out that the results seen in solar cell junctions are similar to those seen by Chynoweth and McKay (204) in very narrow junctions in silicon in which field emission occurs. Shockley and Queisser (201) discount the possibility of these effects being related, since the depletion regions in solar cells, although narrow, are not as small as those studied by Chynoweth and McKay. Since the field emission process is not as yet described by a quantitative theory, it is not possible to demonstrate that this process is not the cause of the anomalous effects observed, in the absence of a reasonably well-established alternative. Queisser and Shockley proposed that the mechanism leading to high A and I_0 values was caused by the presence of undesirable metal impurities in the silicon, introduced either by the use of low-grade silicon starting material, or during the cell processing steps. By examination of I-V curves of diodes cut from commercial cells, it was found that junction areas overlaid by contact regions exhibited characteristics nearer to the ideal. Further, it was shown that heat treatments which might cause precipitation of impurities (and hence their removal from the major active area of the junction), led in some cases to lower A and I_0 values. This precipitation effect was postulated as the cause of the soft reverse characteristics often seen in more efficient commercial cells, a point noted by other workers. However, a specific mechanism was not advanced to connect the postulated impurities and the experimental facts, so that a check on this hypothesis has not been made. In an effort to keep separate the historical account and the evaluation phases of the present research, further discussion on this subject (which inevitably involves some "editorializing"), will be given later.

The comparison of various estimates for maximum theoretical efficiency for solar cells was reviewed by Loferski (200). The conclusion reached was that none of the quantitative theories fitted the facts, and that the mechanisms giving rise to the experimentally

determined I_0 and A values, and the connection between these, were unknown at the time the paper was written (1961). This appears to be the same as the present situation.

3. Power Loss Processes

The fundamental mechanism of operation of the photovoltaic cell has certain power loss processes associated with it which, even in an ideal cell, cannot be eliminated. These determine the ultimate theoretical conversion efficiency, and an account of these has been given in the preceding section. In a real cell, there are other power loss processes present, which, in principle, could be made as small as desired, but which in practice cannot, because of the limitations of technology. Considerable analytical work has been done to identify these processes, and to provide means for calculating their effects on cell performance. In this section, these loss mechanisms will be qualitatively described, and this description will be followed by a historical review of the analyses which have been performed.

Radiant energy impinging on a real solar cell undergoes a series of transformations before emerging as useful work output from the cell, and at each of these transformations, a proportion of the energy is lost. For the purpose of the present discussion, these processes are summarized in Figure 33; referring to the numbers on the chart:

① Optical reflection at the front surface of the cell is assumed zero in ultimate efficiency calculations and is, in fact, made small (3 to 5%) in the main sensitivity range of the cell by the application of antireflection coatings, whose action is described by well-known optical principles (205).

② , ③ , and ④ Electron-hole pair production by the absorption of photons occurs with a quantum efficiency of as close to unity as can be determined in a normal cell. However, under sunlight illumination, the majority of photons absorbed possess more energy than necessary to create hole-electron pairs, and this excess energy is lost by phonon creation. This is a fundamental loss mechanism, which enters into all ultimate efficiency calculations as described in the previous section of this report, and which in effect causes a loss of voltage.

⑤ In ultimate efficiency calculations, the cell is assumed to be sufficiently thick to absorb all incoming photons by carrier pair creation. The actual thickness required in practice to effectively achieve this result varies with the optical absorption constant of the semiconductor used. For silicon cells, a thickness less than about 16 mils causes measurable losses in short-circuit current partly because an appreciable number of photons pass through the cell to be absorbed in the back contact. (If this is opaque, as is normally the case; if the contact covered only a portion of the cell back, some of these photons would be internally reflected at the silicon surface, the remainder would be lost by transmission out of the cell.) Some efforts have been made to reduce this loss by the provision of an optically reflecting back contact, but this

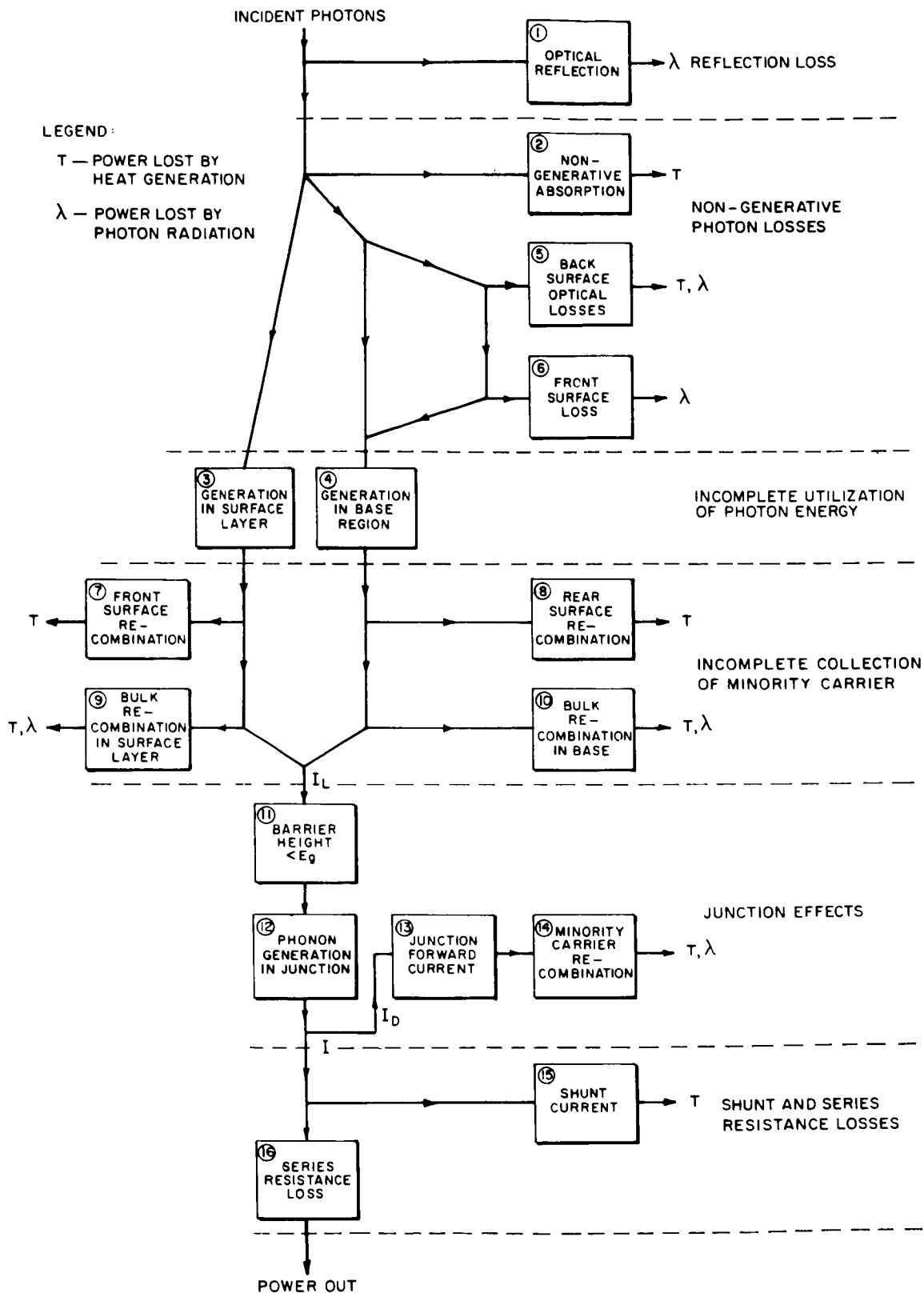


Figure 33. Energy flow chart for a p-n junction photovoltaic cell

appears to be incompatible with the requirement for a low-resistance ohmic contact. In the diagram, photoemission from the back contact has been assumed to be negligible, which is justifiable since in practical cells only low-energy photons reach this region, whereas photoemission normally requires rather large energies, and is also normally characterized by a low quantum efficiency.

⑥ Any photons reflected from the back surface make a second pass through the cell, some being absorbed to create carrier pairs, some being lost by passing through the whole cell thickness and out through the front surface.

⑦ Recombination of minority carriers by way of surface-states is an appreciable loss mechanism which has been given considerable attention by many workers. Since the surface region is very thin, diffusion of minority carriers to the surface would be appreciable, if no fields existed in this region. However, in cells which have the surface region made by the diffusion process, an impurity concentration profile exists such that a field is present which aids in diffusion of the minority carriers away from the surface and toward the pn junction. This effect has also been thoroughly examined by theoretical analyses.

⑧ Since the back of most cells is covered with an ohmic contact at which the minority-carrier lifetime is theoretically zero (and in practice very short indeed, 10^{-12} seconds or less), minority carriers which diffuse to this surface are rapidly lost by recombination. This process is the second factor contributing to loss of current when cell thickness is reduced: cf. ⑤ above. It has been given considerable analytical attention.

⑨ and ⑩ Bulk recombination (which in the diagram also includes recombination in the depletion region) may occur by several mechanisms, some of which are fundamentally necessary, some of which are, in principle, avoidable. These processes have been fully discussed in the previous section of this report.

⑪ In the ideal cell, the barrier height of the junction is equal to the energy gap of the semiconductor. In practice, it is less, by the amount $\Delta E = E_1 + E_2$ shown in Figure 34. This effect is minimized by providing large carrier concentrations in both n- and p-type regions by high donor and acceptor impurity concentrations (other cell parameters being equal). This effect is seen in real cells, being the reason why silicon cells made on 1-ohm·cm base material show better voltage values (for both V_m and V_{oc}) than cells made on 10-ohm·cm base material. This point has received analytical consideration since the original efficiency analysis of Cummrow.

⑫ The separation of hole-electron pairs by the junction depends on the carriers moving to a region which minimizes their potential energy. This "sliding down a potential hill" process generates phonons, and is a fundamental necessity in a cell (except for operation at absolute zero of temperature, where in theory it tends to zero). The actual amount of energy lost this way is determined by the I_0 value of the junction, which has been discussed in the previous section.

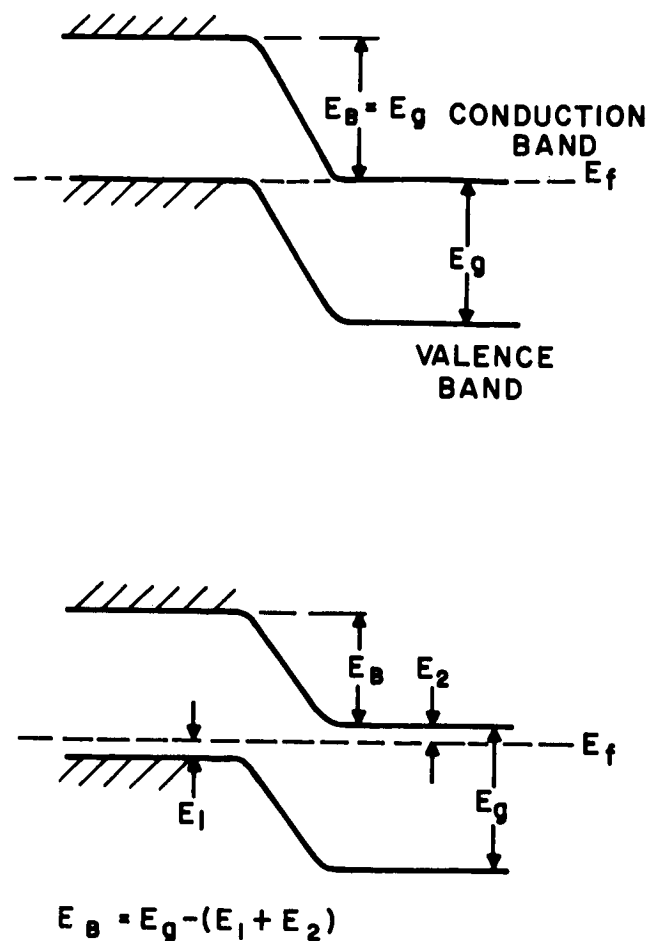


Figure 34. Band diagram showing the effect of low carrier concentration in reducing V_{oc}

(13) and (14) Some forward current in the junction is always present even in ideal cells. The actual amount of energy lost this way is determined by the value of I_0 , which has been discussed in the previous section of this report.

(15) Leakage across the junction may be caused by imperfections in the junction, especially at the edges where ohmic conduction paths are easily formed. A related phenomenon with very different causes is the current caused by recombination in the depletion region, or by any of the other suggested additional-conduction mechanisms in the junction, such as field emission or tunneling. Some of these processes have been discussed in the previous section.

(16) Series resistance arises in a real cell by contributions from various cell regions. In silicon cells the largest contributor is usually the diffused surface region, which contributes a distributed resistance. Some analytical treatments have been

developed for this as a distributed element, but it has more usually been treated as a lumped circuit element. The development of gridded cells, as described in IV-B-1 has helped to reduce the magnitude of the losses from this contribution, and an analytical treatment of the effects of the grids has also been given. Other contributors to the total series resistance of a cell are the base-region resistivity, and the contact resistances. These can accurately be considered as lumped circuit elements, and have been always treated this way.

The way in which methods for the analysis of these effects have been developed during recent years will now be reviewed. The earliest theoretical efficiency calculations of Cummerow, Rittner, Chapin and others made note of the ways in which departures from the ideal cell would lead to lower efficiencies, but quantitative analyses for these effects were generally not given.

The calculation of the dependence of I_{SC} on wavelength of incident light (i.e., the spectral response) received the earliest complete treatment. The problem is conventionally approached by a one-dimensional analysis considering the spatial variation of minority-carrier generation with depth in the cell, using Lambert's law of absorption. The proportion of these carriers which reach the junction is calculated by applying the diffusion equation, with boundary conditions such that the minority-carrier density at the junction plane is zero, and with a recombination velocity at the front and back planes of the cell to account for the surface recombination. An integration is applied over the n- and p-regions of the device to obtain the I_{SC} value for a given wavelength. To obtain the I_{SC} value when a cell is operated under broad-band illumination, this calculation must be repeated to obtain a collection efficiency value for each wavelength used for the illumination (to allow for variations in optical absorption constant with wavelength), and a summation must then be performed to account for the dependence of illumination intensity on wavelength.

A complete analysis of this type was first published by Cummerow (166), although some assumptions on surface recombination effects made in this paper are not those described above. Cummerow assumed a reflecting surface for minority carriers at an ohmic contact, probably because an n-to-n⁺ transition (or p-to-p⁺) gives a field which will tend to prevent minority carriers from reaching the contact region. Thus, the minority carriers are prevented from reaching the zero minority-carrier lifetime region, which is contrary to the assumptions of other workers. In reality, it seems likely that although some field-assisted diffusion away from the contact occurs, the process provides only a small departure from the infinite-recombination-velocity condition usually assumed.

Harten and Schultz (206) used a similar analysis to that given above to show that the surface recombination velocity and minority-carrier diffusion length can be determined from spectral response measurements; the same point was made by Subashiev in 1960 (207) and by Loferski in 1961 (208).

The collection efficiency problem was analyzed by Rappaport, Loferski, and Linder with reference to the electron-voltaic effect (182), and the same analysis was then applied to photovoltaic cells by Loferski in 1956: the approach is that outlined above. Bir and Pikus (209) performed essentially the same analysis as Cummertow, and appear to have been the first to point out that the collection efficiency is maximized if a very shallow junction is used, when account is taken of surface recombination. This is one of the fundamental design philosophies for present-day cells. It should be noted that the work of Cummertow, Harten and Schultz, and Bir and Pikus, was all concerned with germanium cells. Prince and Wolf (193, 194) applied the above-outlined method in detail to silicon cells, and gave a complete derivation and solution for the relevant equations, in 1958 and 1960. The collection efficiency problem was analyzed using the above methods by Moss (210) and by Kleinman (211) in 1961, with special reference to comparing GaAs and silicon cells. The results from the two authors are divergent, Moss showing GaAs superior to silicon, Kleinman showing the converse. The difference arises from surface recombination effects, which particularly influence the performance of cells made with a material having a high optical absorption constant (as GaAs), since all carriers are generated close to the surface. As noted by Kleinman, however, the surface recombination effect does not affect GaAs cells as much, in practice, as one would expect from the analysis. This may be explained in part by field-assisted diffusion in such cells, as discussed below. Kleinman's approach to solution of the collection efficiency problem is interesting in that the functions for the spectral distribution of the incident light and the variation of the optical absorption constant with wavelength for the semiconductor, are both contained in a single expression which is integrated to obtain the overall collection efficiency, thus reducing the numerical integration steps.

The calculations up to 1960 had all assumed that minority carrier motion occurred by field-free diffusion. In 1960, Subashiev and Pedyash (212, 213), Moizhes (214), and Jordan and Milnes (215) independently published analyses showing the effect on minority carrier diffusion of the field produced by the non-uniform impurity concentration in diffused layer silicon cells. These calculations were based on the fact that an ionized impurity concentration change from n_1 to n_2 causes a potential difference of V volts where

$$V = \frac{kT}{q} \ln \left(\frac{n_2}{n_1} \right) \quad (121)$$

Although the actual potential change is small (~ 0.3 V), the field gradient is large because the potential change occurs across the thin surface region, causing fields of up to a few thousand volts per centimeter. A related analysis showing the effect of the diffusion impurity profile on the capacitance-voltage relationship for the junction was given by Lawrence and Warner (216) in 1960, but the analysis involved the use of numerical methods, so that the main value of the work lay in showing the regimes in which the graded and step junction approximations were reasonably accurate. Dale and Smith

(217) performed another analysis for spectral response including the surface-field effect, and also including a short minority-carrier lifetime in the surface region: the authors then applied the analysis to determine the surface recombination velocity and lifetime from spectral response measurements. This work therefore is a refinement of the measurement methods developed by Harten and Schultz (206), Subashiev (207), and Loferski (208), mentioned above.

In 1963, Wolf (218) showed that the effect of field-assisted diffusion in the surface region could be approximated with good accuracy by using a field-free analysis with the minority-carrier lifetime increased by a factor of ~ 4.4 , thus enabling the simpler original analysis to be retained. This appears to be the present status concerning collection efficiency theory: one might add that extremely close agreement is now obtained between theory and practice for most cell types, the notable exception being CdS cells, where the fundamental operation of the device is not fully understood. The effect of reducing the cell thickness was analyzed by Wolf (193, 218), by insertion of appropriate boundary conditions into the solution of the differential equations for the collection efficiency. The correlation between this theory and practice was examined by Wolf and Ralph (219, 220), who found the current to fall with reduced cell thickness more rapidly in practice than would be expected theoretically. More recently, however, this correlation has been re-examined by Crabb and Treble (221), who found better agreement with the theory. Both groups of workers felt that the experimental results of Wolf and Ralph may have been caused by work damage extending into the base from the back contact of the cell, thus reducing the effective thickness of the device.

The second major loss factor which has received considerable theoretical evaluation is the effect of series resistance on the cell operation. Two areas of work are included here, one of which deals with the calculation of power losses caused by lumped-element effects, the second dealing with the effects arising from the distributed nature of the thin surface layer. It may be noted that both of these aspects received initial attention from Schottky during the 1930's (see II-2-b).

The equivalent lumped-element circuit for the cell is as shown in Figure 35(a) for the ensuing account. Since R_s was a major cause of power loss in the initial cells made at Bell Laboratories, it is natural that it should be mentioned in the early reports of Chapin, Fuller, and Pearson (124), although their paper did not give a formal analysis. The point was taken up in detail by Prince (145), who by conventional analysis from the circuit of Figure 35(a) showed that the cell characteristic is given by:

$$\ln \left(\frac{I + I_L}{I_o} - \frac{V - IR_s}{I_o R_{sh}} + 1 \right) = \frac{q}{kT} (V - IR_s) \quad (122)$$

From this, a family of I-V curves was calculated, showing the effect of various values of R_s and R_{sh} , which demonstrated graphically the value of reducing R_s . Neglecting R_{sh} (which is reasonable for most silicon cells), analysis showed that the power generated by the device is given by

$$P = -IV = -I \left[\frac{kT}{q} \ln \left(\frac{I + I_L}{I_o} + 1 \right) + IR_s \right] \quad (123)$$

Thus, the power lost in the series resistance is a separable term in this treatment, which is an approximation valid for R_s small. Prince calculated a curve showing (power output) as a function of R_s . He also tackled the distributed sheet resistance problem by the method illustrated in Figure 35(b), where it is assumed that the "average" point of generation of current is one-quarter of the cell width from the edge. This simplification assumes that the potential variation over the surface of the cell is so small as to negligibly affect the forward current through the junction [I_D in Figure 35(a)], so that the net current contributions from all parts of the cell have the same density. Combining this with the first part of his analysis, and using a very simplified expression for I_L as a function of layer thickness t , Prince calculated a curve showing (power output) as a function of t for a cell 1 cm wide ($W = 1$ cm), with no grids. Hence, an $R_s = 0.5$ ohm and a conversion efficiency of 8% was calculated for the optimum t value ($\sim 2 \mu\text{m}$). Similarly, Prince analyzed the dependence of the (power per unit area) and the (power per cell) on W , showing that there was a width giving optimum value for the former, which for a cell made with the semiconduction parameters measured in silicon, gave $W = 1$ cm for normal sunlight operation. This analysis is for an ungridded cell, but it is related to the grid optimization calculations which came later.

Prince and Wolf (193) analyzed the effects of R_{sh} , using the methods of Prince described above, showing that in practice R_{sh} became significant only when cells were made to operate under low illumination levels. Hence, it was shown that a cell with a deeper diffused surface layer than usual would be better for low-level operation, since junction leakage effects could be minimized by increasing the surface layer thickness.

Wolf (194) provided a very complete analysis of the effects of various losses on cell performance, and followed the treatment of Prince for calculating the loss of power caused by a lumped R_s in the equivalent circuit Figure 35(a). However, gridded cells had now become the standard production type, and Wolf analyzed the effect of the grid geometry on the contribution of the distributed surface-layer and grid lines to R_s . The treatment followed the approximation of Prince in assuming an "average" current generation point one-quarter of the unit field width ($S/4$) from the grid line, as in Figure 35(b). However, Prince's cell now became, in effect, one "field unit" in the gridded cell, as shown in Figure 36. Using the same reasoning as was applied to the surface layer R_s contribution, the "effective length" of the grid line is taken to be $W/2$ for subsequent analysis. (Note that Prince's W has become Wolf's S .) Wolf then performed an analysis which resulted in expressions for the values of W , S , and T which would minimize R_s .

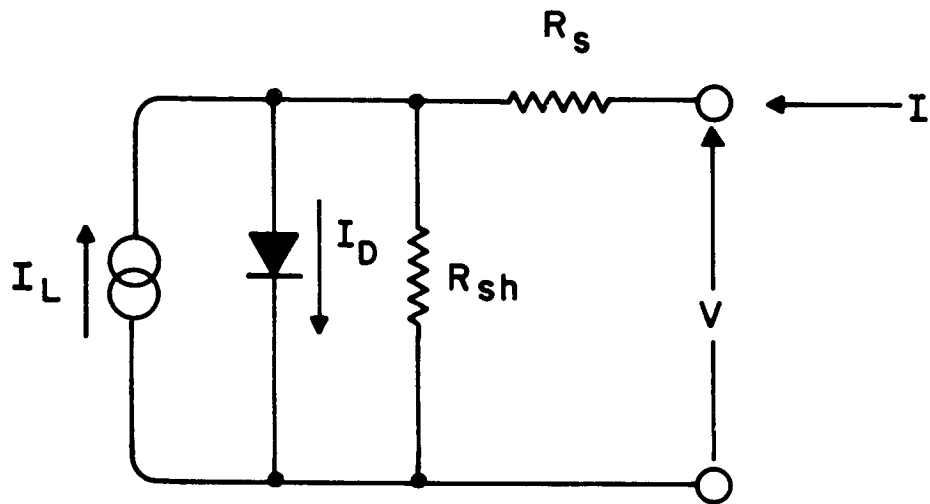
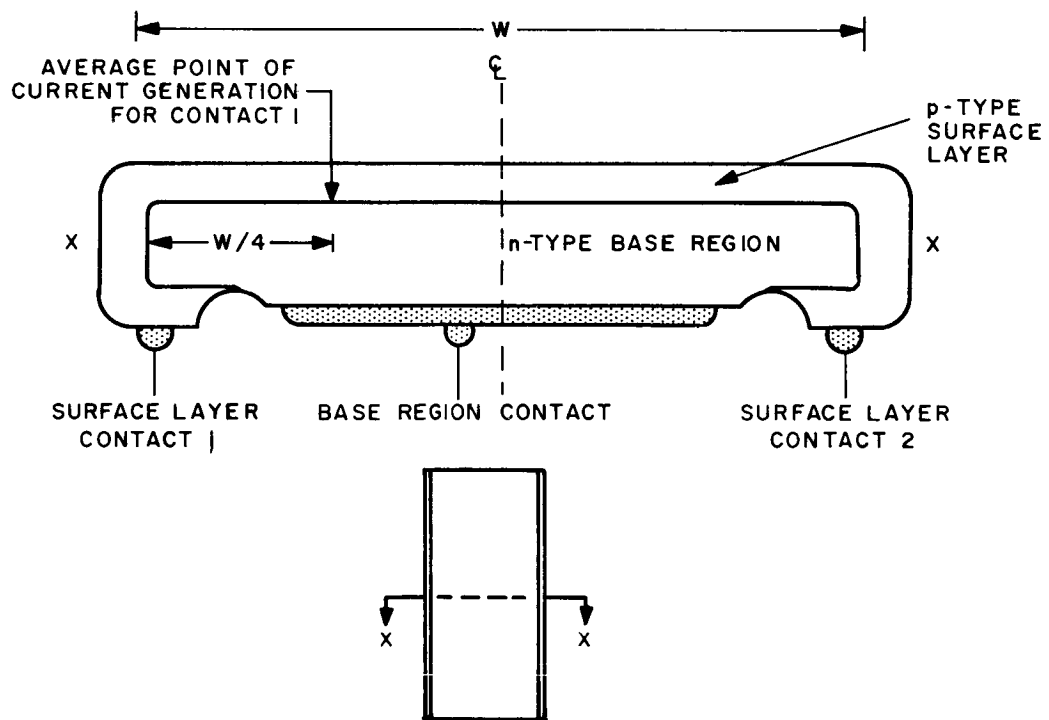


Figure 35(a). Equivalent circuit for a solar cell



CROSS-SECTION THROUGH RECTANGULAR CELL :

Figure 35(b). Cross section of a solar cell, showing dimensions as used by Prince for R_s calculation

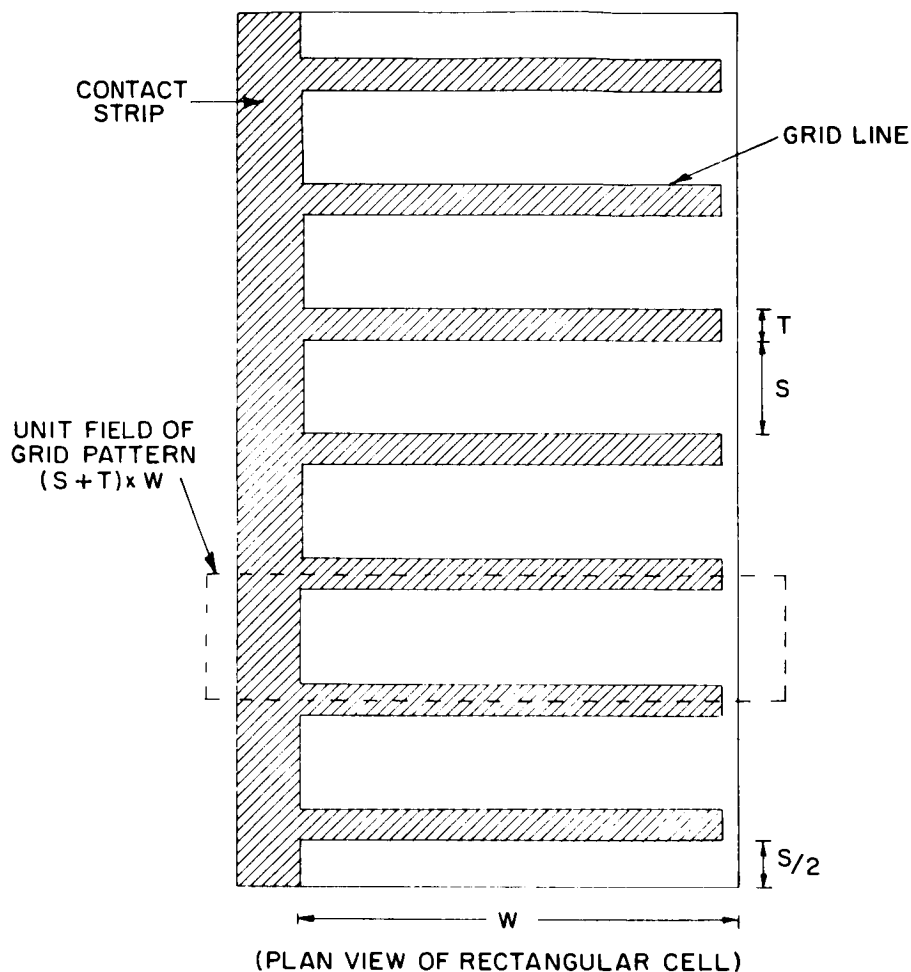


Figure 36. Cell geometry used by Wolf for R_s calculation

This analysis is in error in the assumption that minimizing R_s maximizes cell efficiency (since altering the cell dimensionally alters the output current flowing through R_s , and the power loss is determined by $I^2 R_s$). This point was picked up by Lamorte (222), who provided an alternative analysis in which the power per unit area was maximized by allowing the grid spacing to vary, the grid line width remaining constant (i.e., S variable, T constant in the nomenclature of Figure 36). Lamorte assumed a linear variation of voltage over the cell surface, a questionable assumption justified by experimental measurements on GaAs cells, but a necessary one to provide a tractable analysis. Lamorte's analysis also neglects the resistance of the grid line, which may be justified for small solder-dipped Si and GaAs cells, but which invalidates the analysis for other cell types (e.g., evaporated-grid silicon cells without solder dip, or thin-film cells of the CdS type). Lamorte also makes no statement as to how the grid line width T should be chosen, a point which will be analyzed later in this work.

Lamorte's analysis proceeds by deriving an expression for power output from the cell in terms of the grid geometry and diode equation parameters and the light-generated current density and cell terminal voltage. This is then maximized by the usual methods, providing an expression giving the optimum S value for a given terminal voltage. However, to obtain solutions for the more general case where the cell operating voltage is also optimized, the calculation must be repeated over a range of terminal voltage values to provide simultaneously optimum values for both S and V . It should be pointed out, however, that the variation of S and V is probably slow in the range of most real cells, so that this lack of generality is not a serious objection to application of the analysis to real problems.

Theoretical calculations showing the effect of R_s on cell efficiency were performed at RCA Laboratories under a Signal Corps contract (191) during 1958-60 with special reference to GaAs cells; this aspect of the work under this contract was later published by Wysocki (223). In this analysis, the sheet resistance was analyzed truly as a distributed effect. It resulted in nonlinear differential equations for which numerical methods of solution were used. From such solutions, Wysocki plotted various curves showing how cell performance was influenced by the sheet resistance of the diffused layer. The same analysis was also reported by Moizhes (214) in 1960.

In 1967, Handy (224) reported the results of a theoretical analysis of the contributions to R_s of the various regions of a gridded solar cell, including an allowance for current paths from the surface layer direct to the contact strip without going through the grid line (see Figure 37), a point assumed negligible by Wolf and by Lamorte. Handy also provided an equivalent circuit for the R_s contributions, which was used in 1963 by Ralph and Berman (225) (with acknowledgment to Handy) as part of an experiment to correlate Wolf's theory for grid optimization with practice. This theory provided an optimum grid line thickness less than that technically feasible, so that this work was not as stringent a test of the theory as it might have been, especially as the experiments showed a scatter in results which was more than large enough to mask the effects being analyzed. This is the present situation with regard to the effects of R_s on cell efficiency.

The remaining practical consideration which has been examined theoretically concerns the impurity concentration in the n- and p-regions. In ultimate theoretical efficiency analyses, it is assumed that the carrier concentration is such as to bring the Fermi level E_f to the band edges in the two regions, so that the barrier height in the junction has a value E_g , as shown in Figure 38(a). In practice, the situation is usually as shown in Figure 38(b), and this has two effects:

- (i) At a given voltage across the cell terminals, the junction current I_D in Figure 35(a) is greater.
- (ii) At a given current output from the cell, the voltage at the cell terminals is reduced, and Peltier heating occurs at the cell contacts, caused by phonon generation when the carriers traverse the bent bands at the contacts.

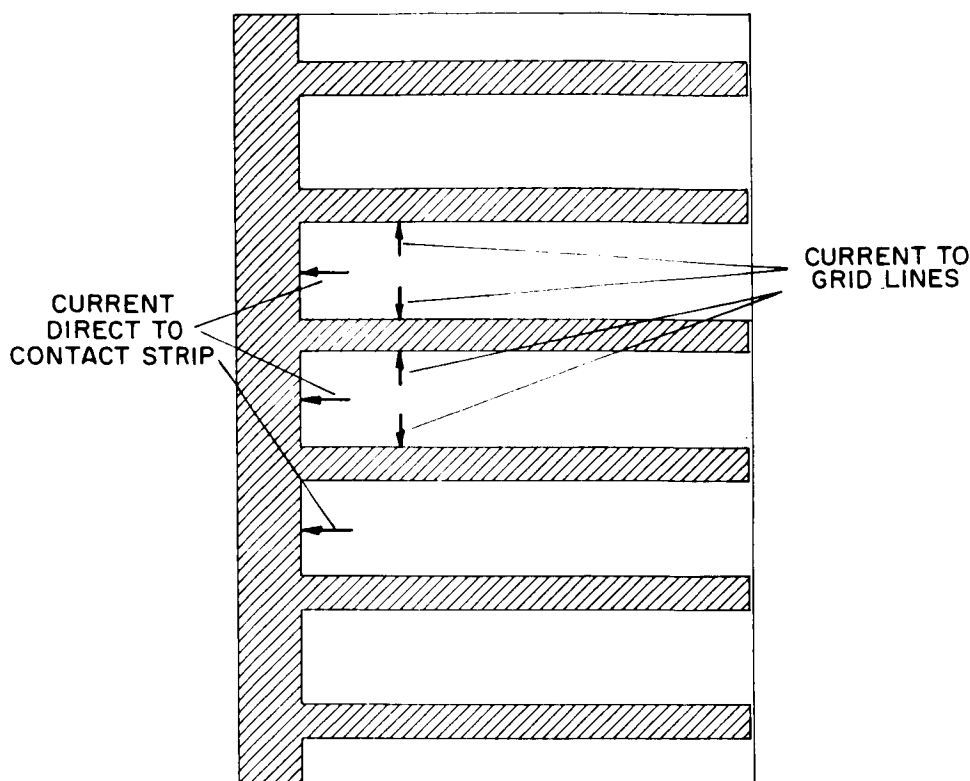


Figure 37. Current paths in a cell, as used by Handy for R_s calculation

At the maximum power point, both of these effects influence the cell operation. The value of heavy doping to produce large carrier concentrations and thus bring E_f to E_c and E_v was pointed out by Cummerow and other early workers, and the results were found in practice when cells made on 10-Ohm·cm resistivity base silicon were made for radiation-resistance testing, such cells exhibiting a V_{oc} and conversion efficiency lower than those of the 1-Ohm·cm cells previously used. The effect of the doping on cell performance received particular attention from Subashiev (212, 213), who pointed out the existence of the Peltier effect in this case. The theoretical and experimental results agree well on this point, so that further work has not been necessary.

In concluding this section, it is perhaps worth pointing out that the papers of Subashiev (213) and Wolf (194) provide comprehensive reviews of the ways in which real cells depart from the ideal.

4. Heterojunctions

Several types of energy-conversion cells based on heterojunctions have been investigated since 1955. These include metal-semiconductor (e.g., Pt-GaAs thin-film cells), degenerate semiconductor-semiconductor (e.g., CdS and CdTe cells), and semiconductor-semiconductor (e.g., GaP-GaAs cells). For these cells, the major research effort has been experimental, but the graded bandgap cell is a special case of a

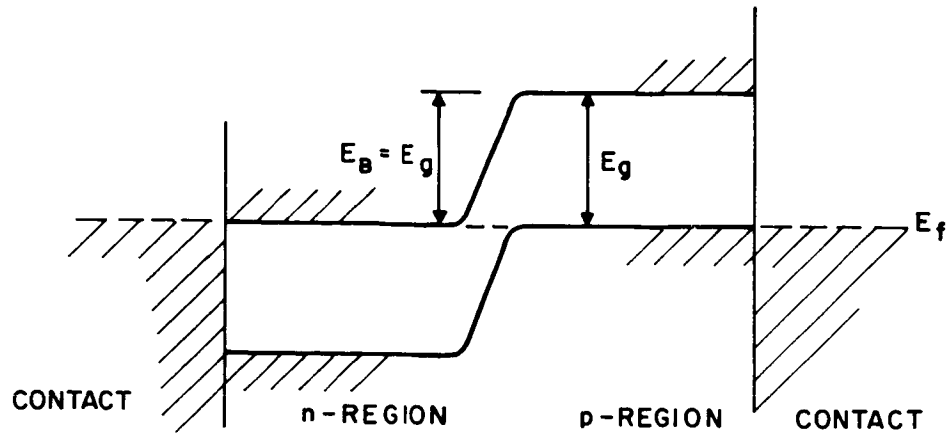


Figure 38(a). Band structure in a photovoltaic junction, barrier height = E_g

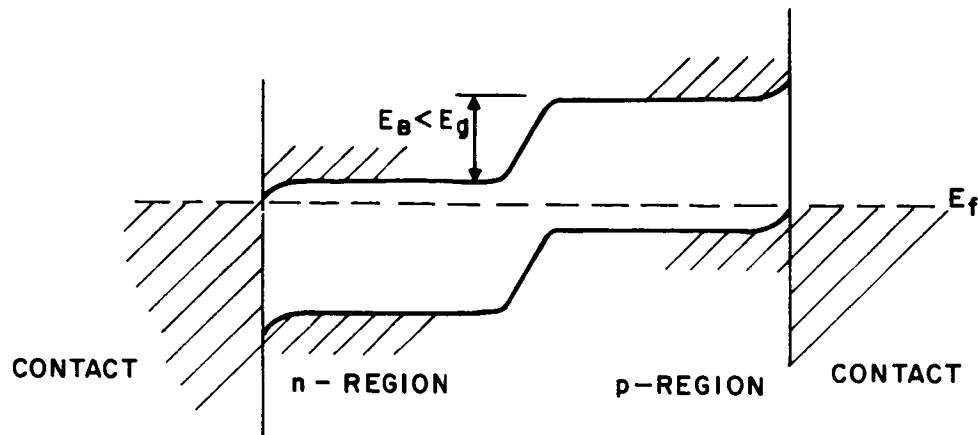


Figure 38(b). The same, barrier height $< E_g$

heterojunction cell, and this has received primarily theoretical attention. In this section, the theory underlying these cells types will be discussed.

An account of the development of the theory of metal-semiconductor contacts has already been given in Sections II-C-2 and III-D-2 above; it appears that this work of Schottky, Mott, and Bethe has received no further development in recent years, aside from the consideration of surface-state effects by Bardeen, as described in III-D-2. A comprehensive and unified account of the present understanding of metal-semiconductor contacts was given by Henisch (226) in 1957. The band structures of an ideal metal-semiconductor junction in equilibrium and under photovoltaic operation are shown in Figures 39(a) and 39(b), with pair creation by absorption of a photon of energy $h\nu$ shown schematically. In Figure 39(a) it is shown that the band-bending at the surface

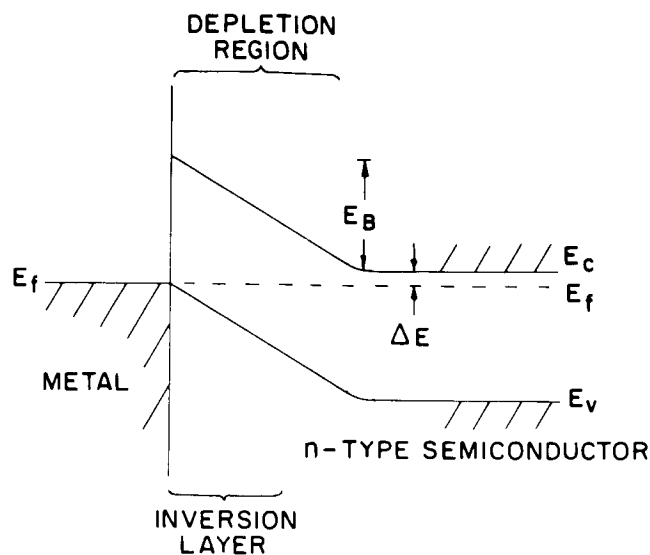


Figure 39(a). Band structure of a surface-barrier cell, equilibrium condition

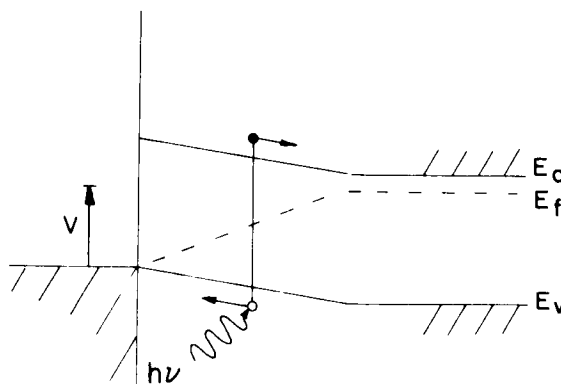


Figure 39(b). The same, under illumination

causes the Fermi level E_f to be closer to the valence band edge than the conduction band edge, thus forming a region of opposite conductivity type. This inversion layer is formed when a blocking metal contact is applied to either a p- or n-type semiconductor, and gives rise to a junction which behaves in many ways as a p-n junction. In particular, under illumination the junction exhibits all the characteristics of the p-n junction photovoltaic effect, and the cell theory can be analyzed the same way in both cases, the only change being to insert an appropriate value for I_0 in the diode equation. For the p-n junction, I_0 is as given in Section III-D-2:

$$I_o = \left(\frac{b}{1+b} \right)^2 \cdot \frac{kT}{q} \cdot \sigma_i^2 \left(\frac{1}{\sigma_n L_p} + \frac{1}{\sigma_p L_n} \right) \quad (124)$$

$$= \left(\frac{b}{1+b} \right)^2 kT (\mu_n + \mu_p) \left(\frac{1}{\sigma_n L_p} + \frac{1}{\sigma_p L_n} \right) \exp \frac{-E_g}{kT} \quad (125)$$

For the metal-semiconductor junction, in the simplest case:

$$I_o = n_{pn} q \left(\frac{kT}{2 \pi m^*} \right)^{1/2} \exp \left(-\frac{E_B}{kT} \right) \quad (126)$$

where

n_{pn} = majority-carrier density in semiconductor

m^* = effective mass of majority carrier in semiconductor

E_B = barrier height as shown in Figure (39)

In practice, surface states are normally present, which have the effects described by Bardeen on E_B (see Section II-D-2), and which probably act also as recombination-generation levels localized at the junction, to cause the effects described by Sah, Noyce and Shockley, as described in IV-A-1. In addition, image forces act to lower E_B , and tunneling may be present, with the effects described by Henisch (226), leading to higher junction currents at small forward bias than would be expected from the simple diffusion theory underlying Eq. (126). Again, the same departures from the diffusion theory are seen in p-n junctions, as discussed in IV-A-1. This is the theory of the Pt-GaAs cells investigated at RCA Laboratories (227), and the surface-barrier Si cell investigated at Tyco Laboratories (228).

A great deal of experimental work has been done on cells made with a Cu_2S -CdS heterojunction, cells made with a Cu_2Te -CdS heterojunction, and cells made with a Cu_2Se -GaAs heterojunction, as described in Section IV-D. The cells on CdTe and GaAs behave in a way which indicates that the degenerate Cu_2Te and Cu_2Se layers behave essentially as metals, merely providing a contact to an inversion layer present at the semiconductor surface. Thus, the theory of these cells is assumed to be that developed for the metal-semiconductor cells described above. For the CdS cells, the behavior is such as to indicate that either the Cu_2S is playing an active role in the cell operation, or a group of trapping levels in the CdS is markedly influencing the photovoltaic behavior. This cell type is a special case, for which an accepted theory of operation has not been developed. An account of the proposed theories is given in the discussion of this cell in Sections IV-C and V-C.

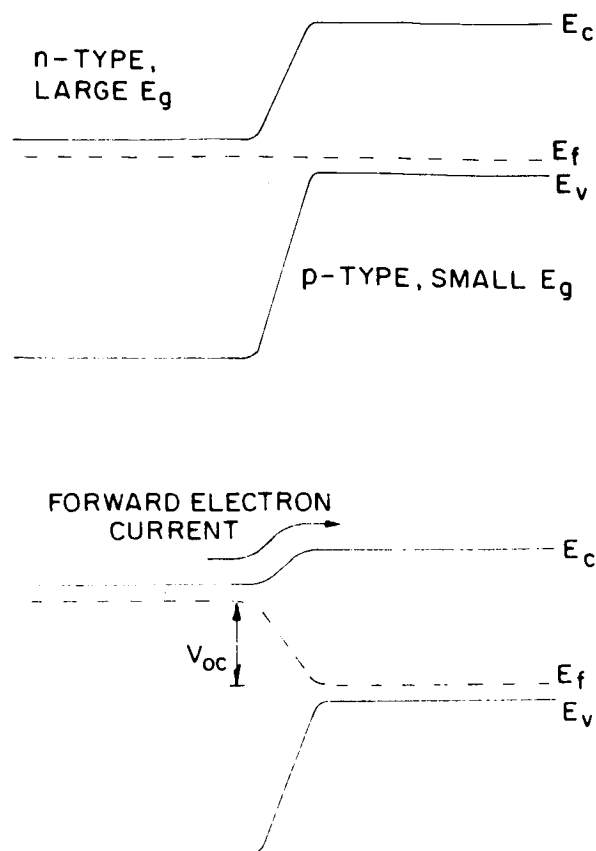


Figure 40. Band structure of a heterojunction cell

The heterojunction cell which has had the most analytical attention is the semiconductor-semiconductor cell. The band-structure of the simplest cell type is shown in Figures 40(a) and (b) in equilibrium and in photovoltaic operation. At first sight, it appears that such a cell may have a higher ultimate conversion efficiency than the single-energy gap cell, since the proportion of the photon energies of the solar spectrum which are converted into hole-electron pair energies is higher. However, as can be seen from Figure 40(b), the voltage developed by the cell is governed by the material with the smaller bandgap, since (in the case shown) V_{oc} is obtained when the electron current in the forward direction in the conduction band equals the light-generated current. (The case of p-type large E_g to n-type small E_g would result in the diode forward current consisting primarily of hole current, the principle remaining the same.) Thus, the device would have an efficiency no higher than that of a cell made with a p-n junction in the small E_g material, as was pointed out by Wolf (194).

A more elaborate type of cell was also considered by Wolf, and (in more detail) by Emtage (229). Emtage considered conduction and photovoltaic processes in a semiconductor with a band-structure as shown in Figure 41(a). Under illumination, a voltage is developed in such a material as was shown by Tauc (230), by a mechanism which

is illustrated in Figures 41(b) and (c). Emtage derived the equations governing current flow in such a device, by considering the transport of carriers in a material with position-dependent conduction parameters. The resulting relationships are complex, and a summary of the results for photovoltaic operation only will be given here; the reader is referred to the original paper for the complete analysis.

Consider the specimen under illumination sufficiently high to bring the electron and hole concentrations into approximate equality. If both carrier types have the same mobility, then the photovoltage developed is as shown in Figure 41(b) for the open-circuit condition, the hole and electron currents balancing, as shown, to give zero net current, and

$$V_{oc} \doteq \frac{E_{g1} - E_{g2}}{2} \quad (127)$$

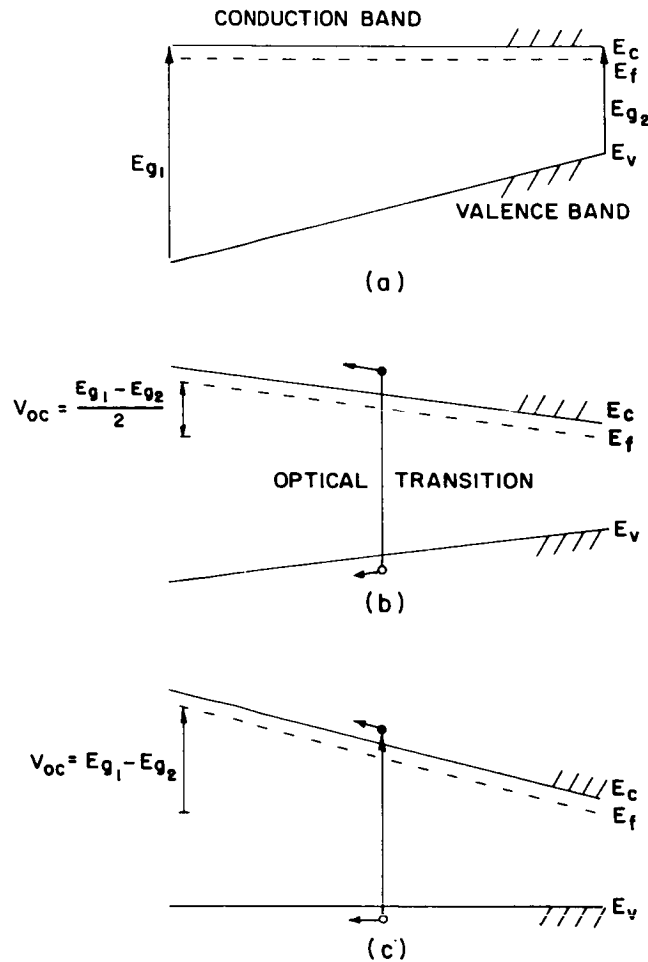


Figure 41. Band structures in a graded-bandgap semiconductor

Now if the hole mobility is much larger than the electron mobility, the open-circuit voltage case is as shown in Figure 41(c), and

$$V_{oc} \doteq E_{g1} - E_{g2} \quad (128)$$

The point made, then, is that at illumination intensities sufficiently high to bring the minority-carrier concentration into approximate equality with the majority carrier concentration, in the case of very different carrier mobilities, V_{oc} can tend to $E_{g1} - E_{g2}$. Now if a p-n junction is placed at the small bandgap end of the device, as shown in Figure 42(a), then a photovoltage tending toward E_{g1} will be obtained under the conditions described above, as shown in Figure 41(c). Emtage then considered a cell made by grading E_g using the GaAs-InAs alloy system, but concluded that the efficiency is only of the order of 20% when the device is operated under concentrated sunlight. If illumination tailored to the particular device were to be used, then the efficiency would improve, which is, of course, true for all cells. The efficiency is roughly the same for the graded bandgap cell and the p-n junction cell with energy gap E_{g2} because the I-V characteristic of the graded

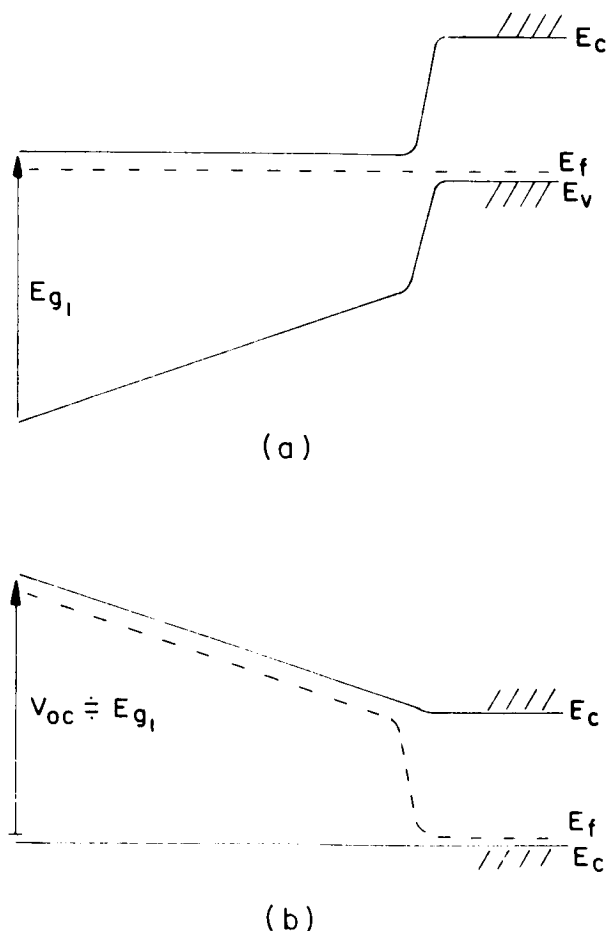


Figure 42. Band structure of a graded bandgap p-n junction cell, (a) in equilibrium, (b) under illumination

region is linear, leading to a total device characteristic as shown in Figure 43. The conclusion reached by Emtage for the conversion efficiency is the same as that arrived at by Wolf, though the analysis is different in the two cases.

The simple band structures used in the analyses of Emtage and Wolf for heterojunctions are not always valid. Oldham and Milnes (231, 232) have considered the I-V characteristics of abrupt heterojunctions with interface states present, and Van Ruyven (233) has used photovoltaic measurements to demonstrate the existence of such states in Ge-GaP heterojunctions.

It should also be pointed out that GaAs cells have been made with a GaP-GaAs heterojunction to allow the active junction to be well below the semiconductor surface, thus minimizing recombination losses via surface states. The theory of such cells has been discussed above; the cell behaves, in principle, as a regular p-n junction GaAs cell, with the same limitation on conversion efficiency, the wide-bandgap GaP merely acting as an optically transmitting conductive layer.

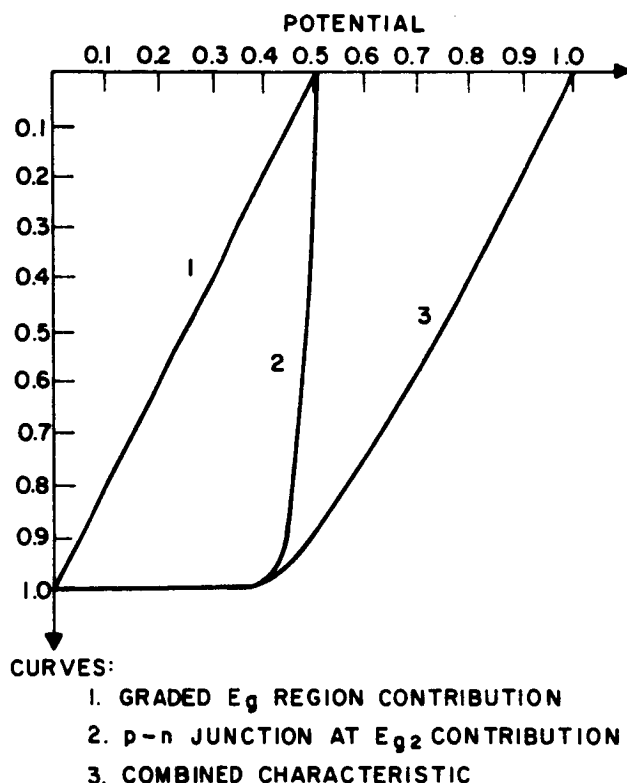


Figure 43. I-V characteristic of a graded-bandgap p-n junction cell

5. The Drift-Field Cell

As described in IV-A-3 above, various workers analyzed the effect of the electrostatic field existing in the diffused surface region from the gradient in doping concentration, to discover whether or not this appreciably affected the collection efficiency of the normal single-crystal silicon solar cell. In 1960, Wright (234) suggested that a similar drift-field might be built into the base region to aid in the collection of minority carriers in a cell whose diffusion length was reduced by irradiation. This point was taken up by Wolf (218) in 1963. The analysis was an extension of that for the field-free cell, published in 1960 (194). The starting point for the calculation was the continuity equation for minority carriers, in which the spatial variation (assumed uni-dimensional) was expressed in terms of generation by photon absorption, loss by recombination, and divergence of minority carrier current density. This was combined with a charge transport equation containing both drift and diffusion terms, resulting in a differential equation which was solved with various boundary conditions. The resulting expression is particularly lengthy, and the reader is referred to the original publication for the details of the derivation. This account will be limited to a discussion of the underlying assumptions and the results of the analysis.

The device geometry used in the calculations is as shown in Figure 44, with two regions on each side of the p-n junction. This two-layer model, which was extended to three layers in the base region, permitted the calculation to include different values of drift field, minority carrier life-time, and mobility in the various regions of the cell. This is an approximation to the real situation, since the minority carrier lifetimes and mobilities are governed by the doping concentration. A region with a constant electrostatic field contains an exponential distribution of dopant, and hence the minority carrier lifetimes and mobilities would vary continuously throughout a region with a constant field, rather than being constant as assumed. However, this simplification is necessary if tractable results are to be obtained. The three-layer model permitted a step-like approximation of the real case of graded material values, and thus allowed an estimation

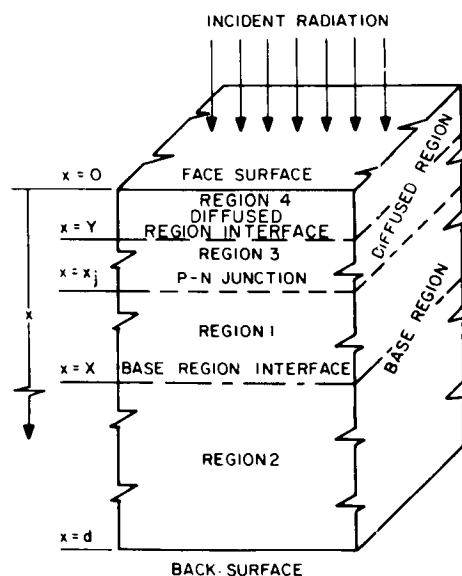


Figure 44. Device geometry considered in drift-field cell analysis, after Wolf (218).

of the effect of their variation within a region. Boundary conditions were chosen to allow for an infinite surface recombination velocity at the base region contact, and a finite surface recombination velocity at the top surface of the diffused region.

The major results of the calculations showed:

- (a) the effect of the drift field in the diffused region on the collection efficiency is indistinguishable from that resulting from an increase in the surface region minority carrier lifetime by a factor of 4.4.
- (b) that by appropriate choice of field strength from impurity density gradient and field region thickness, the radiation resistance of the cell can be optimized for various integrated flux levels, as shown in Figure 45.
- (c) improvement in radiation tolerance by a factor of at least 5 in integrated flux to reach a J_{SC} value equal to 75% of the initial value, compared with field-free cells, can be achieved.

The same type of analysis was performed independently by Cheslow and Kaye of EOS, and also reported in 1963 (235) under a contract sponsored by the NASA (see Table XVII in Appendix III). This used a simpler model than that of Wolf, with only single

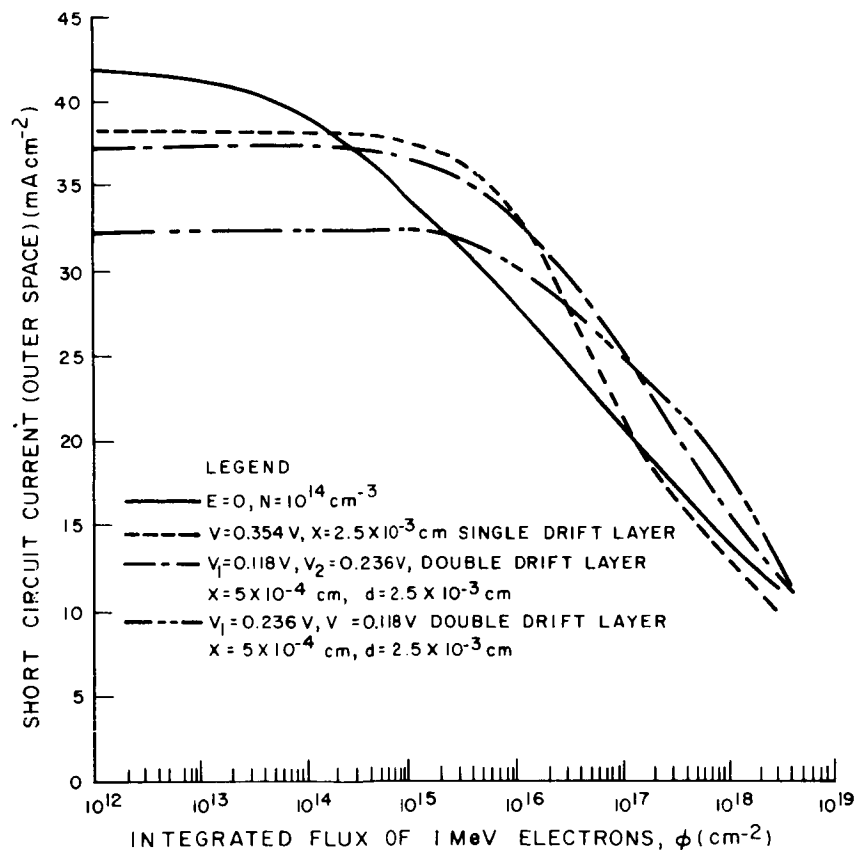


Figure 45. I_{SC} vs flux for 140 mW.cm^{-2} AMO sunlight, showing effect of various drift field configurations, after Wolf (218).

base and diffused regions, and with spatially constant values of mobility, lifetime, and electric field strength throughout these regions. The results were consequently of limited validity, but they also indicated that increased radiation resistance would be obtained in certain cases, and optimization calculations were performed. Many of the results of this work are especially pertinent to thin silicon cells, and are discussed in section IV-B-3.

The major results of this initial work were extended by Kaye and Rolik in 1966 (236), by an analysis in which a linear spatial variation of minority carrier lifetime and mobility, and drift field strength, was permitted. This is an improvement in approximating the conditions existing in real cells, but results in wholly non-analytic solutions to the equation governing carrier collection, thus necessitating numerical solutions by computer. The results of such calculations are as shown in Figure 46, where the increased carrier collection efficiency caused by the drift field in silicon cells with short base region minority carrier lifetimes is apparent. The optimum drift field width was found by calculating the base region collection efficiency as a function of drift field width. The optimum value was found to depend on the base region minority carrier lifetime, and to lie in the range 50-100 μm for lifetimes of the order of 10^{-7} secs., corresponding to a flux of approximately 10^{16} 1MeV electrons cm^{-2} . Experimental evidence supporting this theoretical conclusion was presented, but was obtained with cells in which the drift region field strength was not reported, so that a meaningful comparison with the theory is not possible. In addition, theoretical data correlating the change of J_{SC} with irradiation dose were not presented, so that this point of comparison between theory and experiment also cannot be used.

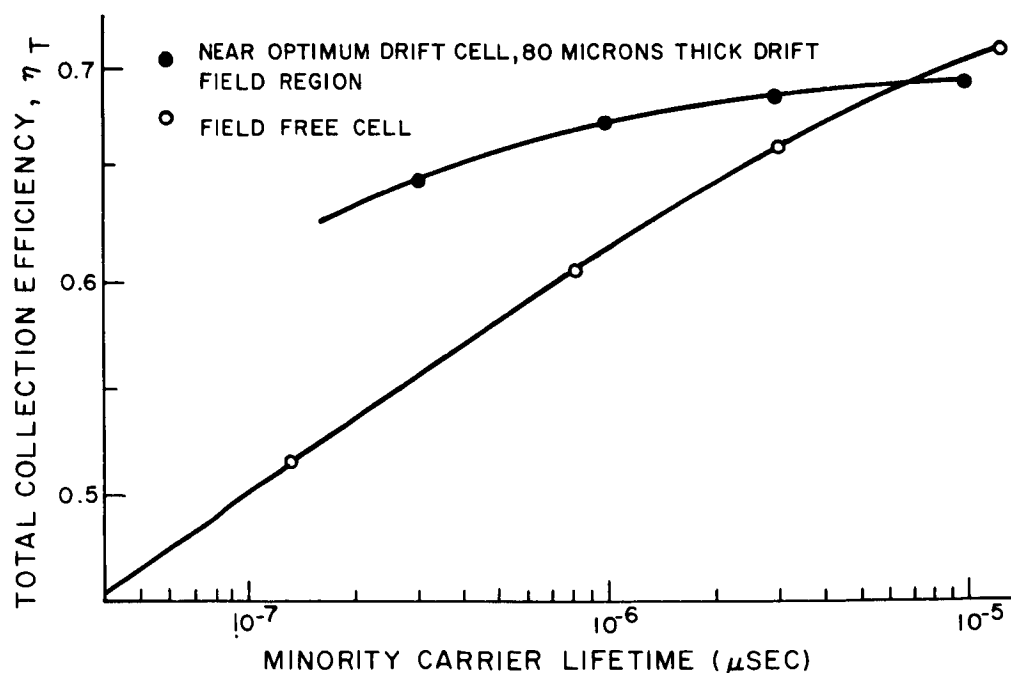


Figure 46. Collection efficiency of near-optimum drift-field cell compared with field-free cell, after Kaye and Rolik (236).

6. The Multiple-Transition Cell

A unique type of solar cell was proposed by Wolf in 1960 (194). In this device, an energy level in the forbidden band of the semiconductor was assumed to be present, such that electrons could be excited from the valence to the conduction bands by two transitions, caused by sequential absorption of two separate photons, as illustrated in Figure 47a. With a single intermediate energy level, a total of three transitions are possible: with two intermediate energy levels, six transitions are possible (Figure 47b). This would in principle allow a semiconductor with energy gap E_g to utilize photons of energy $E_{T1} < E_g$, thus increasing the proportion of photon energy which can be used to generate hole-electron pairs. Wolf calculated that with energy levels chosen to give the optimum match between the cell and the sunlight spectrum, efficiencies up to 50% could be obtained with one intermediate level, and 46% with two intermediate levels (see Figure 48). Wolf pointed out that the intermediate energy level must have rather special properties to allow the cell to operate such as:

- (i) the transition probability for an electron to transfer from the intermediate level to the valence band must be small, i.e., the level must have a small interaction cross-section for holes, when occupied by an electron. This is necessary to allow the electrons to remain in the intermediate level for a sufficiently long time to give a reasonable probability that a second photon can be absorbed to cause transition to the conduction band.
- (ii) the transition probability for an electron to transfer from the conduction band to the intermediate level when this is unoccupied must be small, since otherwise recombination via the intermediate level will reduce the minority carrier collection efficiency.

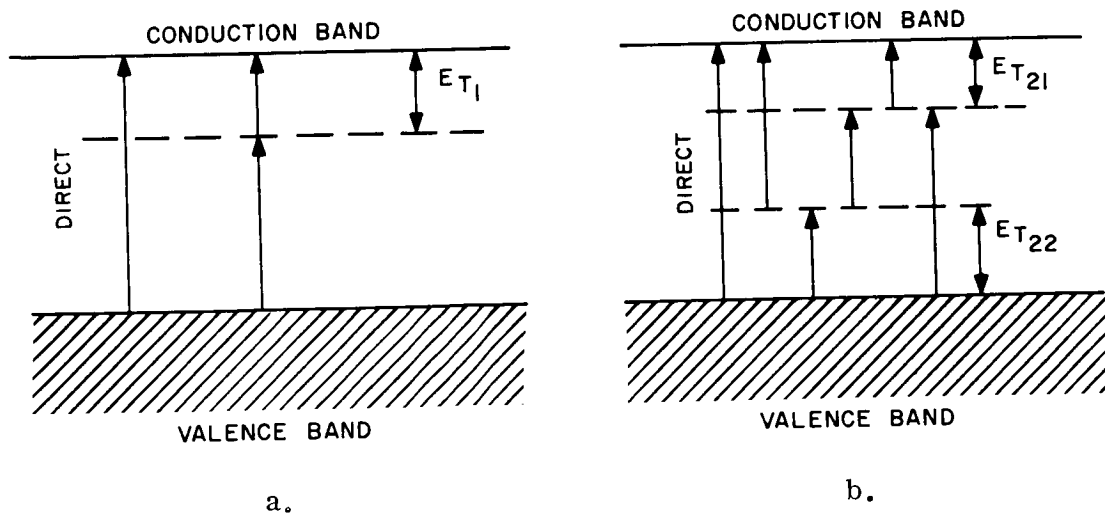


Figure 47. Energy-level scheme for multiple-transition solar cell, (a) single intermediate level, (b) two intermediate levels, after Wolf (194).

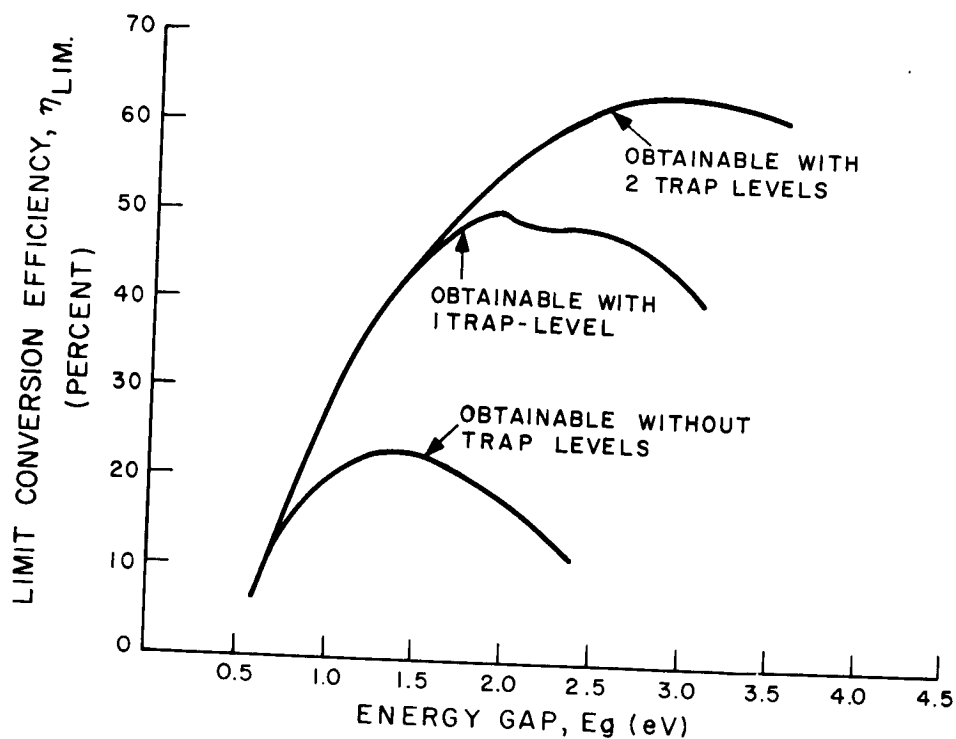


Figure 48. The maximum conversion efficiency for multiple-transition solar cells, compared with the normal cell, as a function of E_g .

Wolf calculated that a density of intermediate levels in the $10^{18} - 10^{19} \text{ cm}^{-3}$ range would be necessary. Both Wolf and other workers have expressed doubt whether such a density of levels can be achieved without significantly impairing the semiconduction properties of the material. There is no doubt that the magnitude of this density is in the borderline range above which such impairment has been observed in many semiconductors. However, so far as is known there is no theoretical objection to the mechanism, which could provide a much more telling argument against the device. It is interesting to note that the two-step photoexcitation mechanism by way of an intermediate energy level was in fact proposed by Reynolds and others as an explanation of the extrinsic response in CdS cells in 1954. Although it appears at the moment that the 1066 or 1067 models describe the experimental situation on present CdS cells rather better, there have been no refutations of the principle of the multiple-transition mechanism.

This has been the only proposal for a cell mechanism which could lead to efficiencies markedly higher than those obtained at the present time in silicon cells. Although there are several unresolved questions relative to this type of device, the potential value of the concept provides a strong urge to further examination of these questions. This point will be taken up later in this report.

B. SILICON SOLAR CELLS

1. Introduction

Before proceeding with the discussion of the development of the solar cell after 1955 it will be useful to introduce some background information. In considering the improvement of the solar cell one must first designate the characteristics or operational parameters of the cell which are both capable of and desirable for change. Taking the most abstract point of view one can consider energy conversion efficiency, weight, cost, and resistance to various environmental factors as the important parameters for improvement. These factors will play an important part in the following discussion of the development of silicon solar cells. A further breakdown and discussion of some of the very general categories listed above will be helpful before proceeding with the consideration of specific photovoltaic cells, such as the silicon cell.

A generalized breakdown of the relative values of the various cost factors involved in the fabrication of a solar cell is not easily obtained due both to some variation in technique and to the tendency of manufacturers to be secretive on this aspect. It is generally agreed that materials form a significant portion of the cost, but little can be gleaned beyond this. It is possible, however, to discuss a number of studies that have been aimed at introducing innovations which would reduce the cost of specific areas of cell manufacture. This includes the use of cheaper materials (i.e., polycrystalline silicon), the production of large-area cells, and the development of new techniques for performing certain specific operations such as junction formation. It is in this relatively unstructured way that improvements in the cost factor of solar cells will be considered in the following discussions.

The weight of the cell itself (ignoring coverglasses and the like for the time being) is rather easily broken down. One has, first of all, the weight of the material (silicon, etc.), the weight of the contacts (grids, busbar, base contact), and the weight of any coatings or encapsulant (antireflection, etc). In conventional single-crystal cells the vast majority of the weight is distributed between the weight of the material and the weight of the contacts. The majority of the programs designed to reduce the weight of the cell have concerned themselves with reducing the thickness of the material.

Under the heading "resistance to various environmental factors" one can lump a multitude of desired virtues; however, for most current cells and uses there is one single factor of overwhelming concern - radiation resistance. Other factors become important for particular missions (e.g., temperature) or particular types of cells (e.g., humidity for some thin-film cells) and will be discussed in context where appropriate. Brief discussions of developments in radiation resistance will be given, where appropriate, throughout the description of solar cell history and development. For more detailed information the reader is directed to the references cited in these discussions.

A dominant requirement for solar cell research during the period these cells have been in use has been efficiency improvement. This has been analyzed in great detail by many workers, and an account of the various factors which determine the conversion efficiency of a solar cell has been given in the preceding Section IV-A-1. The improvement of efficiency has been the main motivation for many of the changes which have been made in practical cells, and an account of these follows.

The following material covers the experimental development of the solar cell from the mid 1950's until the present. Investigations during this period were expanded to cover a wide variety of materials and techniques in the hope of finding new, more efficient types of solar cells. The most important material during this developmental phase has been silicon, and it is this material which will be discussed first. The discussion of silicon is broken into two parts. The first part covers the evolution of the solar cell as it exists today and discusses, for the most part, only those developments which were successful in improving the cell and bringing it to its present state. The second part discusses many of the experimental investigations which were not successful or were not or have not yet been completed. This break was made because it was felt that a more coherent account of the history of the solar cell would result if some of the extraneous material were presented separately.

Many of the research programs aimed at improving silicon solar cells have been supported by the U.S. government; see Table XVII in Appendix III for a summary of these.

2. Development of the Present Cell Types

The introduction of the Bell Laboratories solar battery and the work on the electron-voltaic effect marked the beginning of serious investigations into the development of large area p-n junction devices for energy conversion. At the time of disclosure the maximum efficiency of the Bell solar battery was 6%. Three types of losses were singled out as being major contributors to the discrepancy between the observed efficiency and the theoretically predicted maximum of 22%. These were surface reflection, bulk and surface recombination, and series resistance. Prince's analysis (145) indicated that an important loss factor in earlier cells had been due to series resistance at the contacts. By optimizing the cell design Prince calculated that the series resistance of the cell as it then existed could be reduced to less than 1 Ohm (his test samples had resistances of 2 to 6 Ohms). This would give an increase of 30 to 40% in efficiency. In the same publication Prince also suggested the use of quarter-wavelength type antireflection coatings to improve the efficiency.

Advancements in cell efficiency were rapid during this early period. Within a year after the original announcement of the solar battery, Chapin et al. (144) reported that the best efficiency had increased from 6% to 11%, and that most of the units made were consistently around 8% in efficiency. With the exception of some improvements in contacting the cell, no clue was given about the developments leading to this increase.

An early, technically successful experiment with the application of silicon solar cells to power a remote telephone repeater station, proved the severity of economical competition which photo-voltaic solar energy conversion has to face in earth surface applications in well-developed countries. After the conclusion of this experiment, the interest in solar cells waned at Bell Telephone Laboratories for several years, and the development of silicon cells was carried forward during this interval predominantly by two smaller semiconductor device manufacturers.

In 1955, not long after the announcement of the Bell solar battery, development work on silicon solar cells was started by National Semiconductor Products, a Division of National Fabricated Products, Inc., Evanston, Illinois, which later became the Semiconductor Division of Hoffman Electronics Corporation, El Monte, California. The first efforts were directed toward duplicating the processes and results achieved by the workers at Bell Telephone Laboratories. The following is a description of some of the early work.

Single crystals of silicon were pulled in rf-heated, Czochralski type crystal-growing furnaces, designed as improved versions of those then in use at Bell Telephone Laboratories. DuPont high-purity silicon-crystal needles, produced by the same basic process as described in Section III-B-2, were used as raw material. The purity of this material has been improved through several steps of distillation of the silicon tetrachloride before its introduction into the reduction chamber. However, the ultimate purity of material resulting from this process was limited by the introduction of zinc from the reducing vapor and of boron and oxygen from the quartz lining of the reaction chamber.

The crystals were doped n-type by the addition of arsenic to the melt. The ingots, grown in the (100) direction, were of nearly circular cross section and were cut into wafers in the direction normal to the growth direction of the ingot, using diamond saw blades, of approximately 0.020-in. thickness. In contrast to the cells prepared at Bell Telephone Laboratories at that time, which were of approximately $5/8$ to $3/4$ inch diameter, the cells prepared at National Semiconductor Products were of $1-1/8$ inch diameter.

Diffusion was carried out at approximately 1100°C , using boron tri-chloride in gaseous form as an impurity source. A diagram of the diffusion apparatus is shown in Figure 49. The structure of these early cells was similar to that of the Bell solar batteries, with both contacts on the back side of the cell, separated by a ring area, which was etched into the back of the wafer, and in which the p-n junction came to the surface of the wafer. The contacts were applied by an electroless nickel-plating process similar to that used at Bell Telephone Laboratories. The detailed specifications of this process were later found to be described in the Metal Plating Handbook.

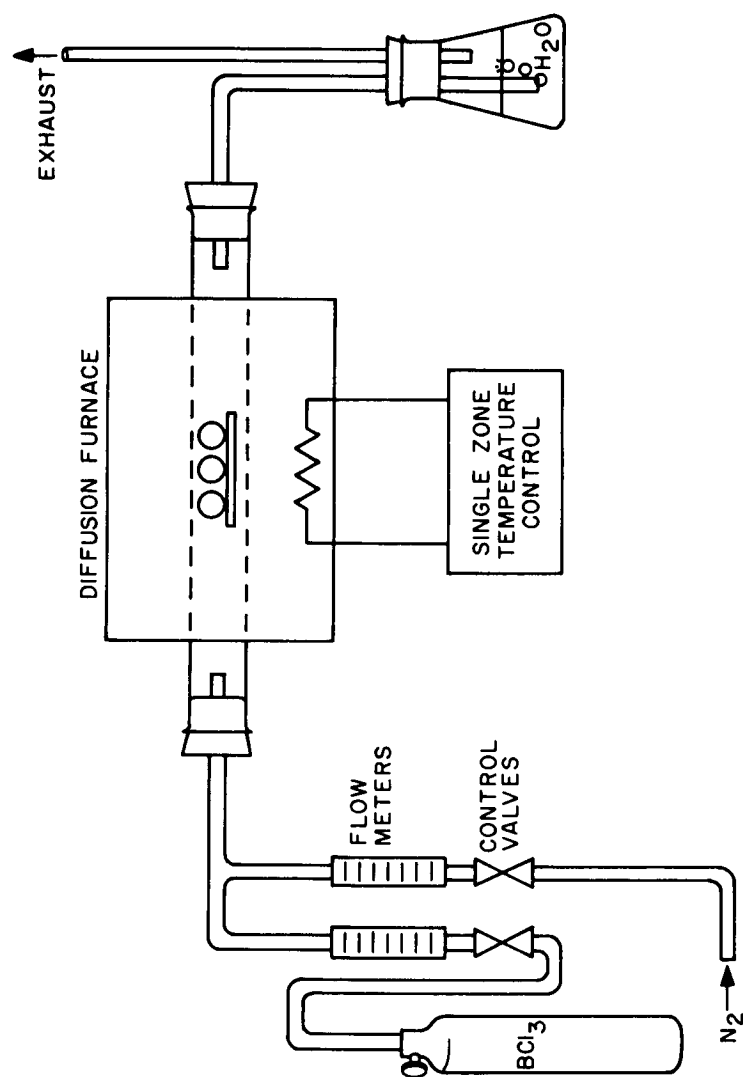


Figure 49. Diffusion apparatus circa 1955

Great difficulties were experienced in bringing the processes, particularly diffusion and contact application, under control. The difficulties experienced with diffusion were partially associated with temperature control, control of the gas ambient, and with impurities contained in the diffusion source. While the first two problems were identified and, at least partially remedied reasonably soon, the third problem was not solved until several years later when a source of higher purity boron tri-chloride became available. Despite these difficulties, by the end of 1955, cells with efficiencies in the 6 to 8% range in earth surface sunlight were obtained. These efficiencies were comparable to those measured on cells fabricated at Bell Telephone Laboratories at that time.

Other early problems were associated with achieving sufficiently high surface concentration of boron to insure that the series resistance of the diffused region was low enough to prevent large power losses. Also, it was soon discovered that the formation of a mysterious surface layer with a velvet black appearance was necessary in order to achieve high efficiencies. While the nature of this layer was not understood, its formation was found to be closely related to the temperature during diffusion, and to the gaseous ambient. Closely connected to this black surface layer was a second, insulating, alloy type layer, which was always formed in the boron tri-chloride diffusion process, and which had to be removed by a subsequent chemical and mechanical process. Occasionally, this second layer would be found to be only loosely adhering to the surface of the wafers, cracking and flaking off some areas during removal of the wafers from the diffusion furnace. In general, this second layer would, upon immersion in boiling concentrated nitric acid for a few minutes, change its appearance from a dark gray solid layer to a yellowish-light gray layer consisting of loose, powdery particles. After drying of the wafer, this layer could be removed by blowing or light brushing with a soft camelhair brush. Very frequently, however, it would be found that this transformation of the surface layer did not take place. Rather, a very tenaciously adhering greenish to medium gray layer would be found over part or all of the surface of the wafer. This layer was opaque to light and electrically insulating. Extensive, repeated boiling in nitric acid would occasionally help to soften this layer, and severe abrasion with stiff bristle brushes was some times partially successful. Otherwise, removal of this layer was in many instances found impossible. No chemical solution, including aqua regia was found which would dissolve this layer. Etching solutions which dissolve silicon would remove the silicon wafer (diffused layer) below this surface layer and let the surface layer float off without dissolving it. This problem of the inert surface layer has plagued silicon solar cell production for several years, and has contributed severely to low yields and high prices. In general, it was found that diffusion at lower temperatures and the careful exclusion of oxygen and humidity in the diffusion chamber would considerably reduce the problem. It was also found that this problem did not occur with some lots of boron tri-chloride, while others produced it consistently.

After diffusion, the process consisted generally in masking the entire wafer except for the central area on the back surface, to an outer diameter of 7/8 inch. This area was somewhat smaller than that to be covered by the ring contact (1 inch I.D.). The exposed area was then etched out to bare the base material. Subsequently, a larger part of the back surface was masked, exposing only the center 3/4 inch diameter circle for a sandblasting operation. The sandblasting abrasive could not be allowed to reach the region where the p-n junction was exposed on the back surface of the wafer, since whenever this happened it caused shunting of the p-n junction. After the sandblasting operation, the back surface masking was removed, the back surface of the wafer cleaned, and new masking material applied to a ring area (3/4 in I.D., 1 in. O.D.) over the region where the p-n junction reached the surface. Next, after a short pre-treatment, the wafer was immersed in the nickel-plating solution, for deposition of the positive and negative contacts. After removal of the masking material and cleaning of the wafer surfaces, the wafer was immersed in a liquid solder bath, in which solder would wet only the metal coated surfaces.

Numerous waxes and cements were tested for use as masking materials. These were found to be attacked by the standard silicon etching solutions, unable to withstand the high temperatures of the plating baths, or difficult to apply or remove. Another experimental approach was to use specially shaped sealing gaskets of rubber, Kel-F elastomer, and Teflon. These gaskets were held in place on the wafers with clamp-like tools, which were designed to provide a low-labor process with permanent masking devices of quick-change capability. Although this approach appeared, at first, attractive from the economy viewpoint, many difficulties were experienced with leakage of etching solution, the sandblasting abrasive, or the plating solution underneath the masking gaskets. This caused high reject rates and destroyed any potential economic advantages.

The application of various die cut tape masks was investigated next. This approach proved successful, after a Mylar base tape with a silicone adhesive was found, which withstood the highly acidic etching solution, the sandblasting, and the highly basic, hot plating solution. A disadvantage was that the tape could not be removed by immersion in a chemical solution, but had to be peeled off manually. This would, however, leave the surface relatively clean since the adhesive would be stripped off together with the tape. This process, experimented with as early as 1955, has proven to be the most successful to the present time.

The next problem was that of controlling the contacting process, which used the electroless nickel-plating technique. In order to obtain a low resistance ohmic contact to the base material, the surface of the latter had to be roughened by sandblasting. Then the wafer was subjected to a cleaning process and immersed into the hot nickel-plating solution. With time it was found, that careful cleaning before plating and meticulous control of the composition and of the temperature of the nickel-plating bath, contributed significantly to the control of this process. The nickel-plating solution contains a large amount of ammonium hydroxide, which would rapidly evaporate from

the bath which had to be maintained near 90°C. Enough ammonia had to be present in the nickel-plating bath to maintain the pH above 9.5. It was found that adding an excess of ammonium hydroxide to the bath, which would cool off by this addition, and immersing the cells when the bath approached the process temperature of 90°C and the pH was still near 10.5 would lead to the most consistent production on strongly adherent low-resistance contacts.

Several experiments were performed using activators, like palladium chloride, to enhance the repeatability of the electroless nickel-plating process and the adhesion of the plated layer. It was found that, although dipping into the activator solutions prior to plating enhanced the deposition process, it by no means improved the adhesion of the plated layer. Rather, it was found that improperly cleaned surface areas which would not ordinarily be covered in the plating solution, could in fact be plated if activators were used, but that the resulting deposits did not adhere well to these areas. These experiments were repeated over a period of several years, and each time the same results were observed. Therefore, as long as the nickel-plating process was used, it was generally carried out without the use of activators, but rather with the exercise of extreme care in the cleaning of the surfaces and of strict control of the plating process.

It may be noted with amusement, that in the early times of semiconductor process technology, difficulties were experienced which were based strictly on the inexperience of human operators with this new technology, and on their disbelief in the critical importance of the control of these processes. For instance, it was found a few times that the contacting process led to bad results despite strict process controls. The reason was then traced to contamination of the abrasive in the sandblasting apparatus which, despite regulations to the contrary, had been used to sandblast a greasy machine part or a sparkplug. Cleaning of the sandblaster and changing its abrasive eliminated the problem.

Difficulties were also experienced with the masking for the sandblasting, the etching and the plating processes. One problem experienced was that the sandblast masking was not sufficiently adhesive to prevent the penetration of abrasive.

Difficulty in applying the mask for the ring areas frequently led to mis-alignment and contributed to low production yields and prevented handling in an efficient production manner. This led then to a change in solar cell geometry. The positive contact was moved to the front surface to form a ring contact which reached to the perimeter of the cell. The p-n junction was exposed at the edge of the cell, and the negative contact covered the entire back surface. This method required protection of only the front surface during the sandblasting operation, and of the entire front and back surfaces during the etching operation, which now was performed after the plating of both contacts. For the latter process it was now only necessary to protect a circular area on the face of the cell in a reasonably concentric manner with the entire back of the cell

exposed. This simplification led not only to considerably better production yields, but also to an increase of the average efficiency of the cells. The reason for this increase was found in the reduction of the series resistance.

On the cells with both contacts on the back surface, the negative contact occupied a circular area of $3/4$ inch diameter. This means that only 44% of the exposed front surface had a negative contact area immediately behind it. The average of the charge carriers generated in the remaining 56% of the front area had to travel a distance of approximately $1/4$ inch in the relatively high-resistivity base material, parallel to the wafer surface in a rather small cross-section, before reaching the contact. This contributed considerable series resistance and degraded the performance of the cells.

Immediately following the change of contact geometry on the circular cells, which was introduced at the beginning of 1956, a change in the cell geometry to a rectangular shape, with the positive contact strip extending along one long edge of the cell, was also introduced. Through these changes and improvements in the production processes, cells with average efficiencies of 6 to 8% were regularly made in 1956, with average efficiencies of 12% being regularly obtained in the laboratory in 1958 on $1/2 \times 2$ cm cells, and of 10% on 1×2 cm cells.

It may be noted, that the entire effort of development of silicon solar cells at that time was directed towards earth surface application. It was vaguely expected, that the introduction of this new energy conversion device would open up a wide range of possibilities for utilization of solar energy. The relatively low energy density of earth surface sunlight was not considered a significant hindrance, but it was realized from the outset, that the solar cell price would have to be low in order to attract large-scale applications. For this reason, emphasis was placed from the beginning on the introduction of efficient production processes and on the search for lower cost raw materials and procedures. The price of the raw silicon material at the time was in the 500 to 600 Dollar per pound range in quantity procurement, and although DuPont projected potential price reductions of well over an order of magnitude for future mass production, prices in that low range have still to be realized.

The purity of the material that was available at that time, also contributed to high costs. The purity was marginal not only from the viewpoint of achieving the desirable resistivity range in the pulled crystals, but also because the excess impurities caused twinning during the growth of the ingots. Frequently, none or only small portions of an ingot could be used because of twinning or deviations from the specified resistivity range, which already exceeded a factor of four. Experiments proved as early as 1956 that cells prepared from wafers with one or two crystal boundaries were generally as high in efficiency as single-crystalline cells. However, cells containing many crystal boundaries, (crystallites under $1/4$ inch in diameter) produced efficiencies of only a few percent or less. For this reason, solar cells containing one or two crystal boundaries were fabricated for some time, effecting a corresponding reduction in the ultimate cell cost, until specifications written for spacecraft application of solar cells eliminated this practice.

A multitude of potential earth surface applications were explored at that time. These included large area solar power panels for providing electrical power for remote forestry observation stations and remote buoys or lighthouses. Power supplies for recharging flashlight batteries were made by mounting a strip of solar cells under a transparent cover on the outside of the flashlight housing (directed at military applications), and a strip of solar cells was incorporated under a clear plastic cover on the top of an Army helmet, to power a communications radio set contained on the inside of the helmet. Also explored were the application of solar cells to power transistorized radios and even record players, and thousands of cells were delivered around 1958 to be mounted on the outside of frames of spectacles which contained hearing aids.

With the majority of the interest directed toward finding significant earth surface applications for solar cells, it is not surprising that a small procurement by the U.S. Army Signal Corps Research and Development Laboratory for a few hundred $1\frac{1}{2} \times 2$ cm solar cells, to provide power on the first Vanguard Space Satellite, did not arouse much attention. Even when, in 1958, the same group placed the first larger order for several thousand 1×2 cm solar cells to provide the various interested government agencies with a small stockpile of solar cells, the huge potential for solar cells in space was hardly recognized.

The early solar cells produced by Bell Laboratories and others were made by diffusing boron into n-type silicon wafers. In 1956 the first Russian publication on solar cells appeared (237). The Russian workers (Maslakovets et al.) used p-type silicon and diffused antimony into the surface to form a p-n junction. The reason for studying n-on-p cells, as stated by the authors, was twofold. The first was a matter of scientific interest as a contrast to the work which had been done by the Bell Laboratories people. The second was that the Russian manufacturing methods yielded silicon which was predominantly p-type, making this type material considerably cheaper and more readily obtainable than n-type silicon. Maslakovets et al. experimented with both single-crystal and polycrystalline cells. The polycrystalline cells were studied to evaluate the possibility of manufacturing cells with efficiencies of 1% to 2% out of relatively impure silicon ($\rho < 1 \text{ Ohm}\cdot\text{cm}$). The efficiencies obtained on the polycrystalline cells were not encouraging, being less than 0.6%. The single-crystal cells were made from 5- $\text{Ohm}\cdot\text{cm}$ material with a quoted minority carrier lifetime of $4 \mu\text{s}$. The maximum efficiency achieved (under a solar intensity of $91 \text{ mW}\cdot\text{cm}^{-2}$) was 2.8%. This cell had an open-circuit voltage of 0.45 V and a short-circuit current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. This work indicated that the Russians, for economic reasons, were working with n-on-p cells long before anyone realized the radiation-resistant virtues of this particular structure.

At the conference on photoelectric effects held in Kiev in 1957 two papers dealing with the Russian work on silicon solar cells were presented. The first, by Tuchkevich and Chebnokov (238), gave a few of the details concerning the construction of the n-on-p cells. A typical cell is shown in Figure 50. The junctions were diffused to a

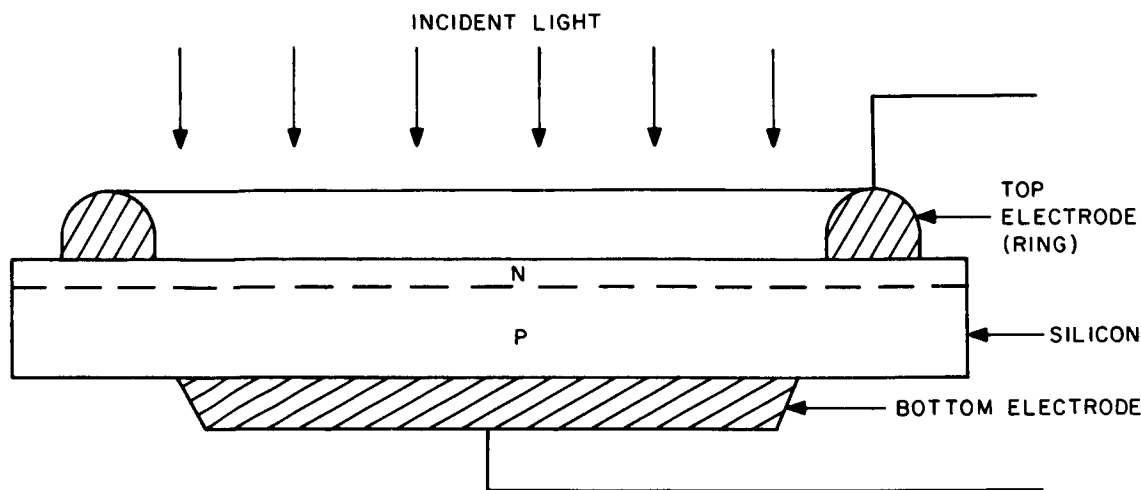


Figure 50. Sectioned solar cell after Tuchkevich and Chebnokov.

depth of 15 to 20 μm and the cell was then etched to give a junction depth of 5 to 10 μm . Soldered contacts were used and the series resistance due to these contacts was approximately 2 Ohms. Under a solar intensity of $80 \text{ mW}\cdot\text{cm}^{-2}$ one of the cells whose I-V characteristic was shown, had an efficiency of 8%. This cell had a short-circuit current density of $22 \text{ mA}\cdot\text{cm}^{-2}$ and an open-circuit voltage of about 0.47 V. Another of the cells, measured under a 2700°K color temperature tungsten lamp, had an efficiency of 9.5% at $100 \text{ mW}\cdot\text{cm}^{-2}$ intensity and 10% at an intensity of $120 \text{ mW}\cdot\text{cm}^{-2}$. Measurements were made of minority carrier lifetimes of 1 to 100 μs for electrons in the p-type material and less than 1 μs for holes in the n-type material. Better efficiencies were anticipated if recombination losses and the series resistance could be reduced. The temperature dependence of the open-circuit voltage was found to be linear, with a slope of $2.57 \times 10^{-3} \text{ V}\cdot(^{\circ}\text{C})^{-1}$. Extrapolation of the temperature dependence data gave a value of 1.1 eV for the gap energy. Measurements of the open-circuit voltage as a function of short-circuit current (light intensity) indicated that the ideal diode equation was not obeyed and a constant term had to be introduced in the exponential to account for this. The plots of open-circuit voltage versus the logarithm of short-circuit current showed three distinct linear segments. The first and third segments of the room-temperature plot, corresponding to low and high intensity respectively, required a constant in the exponential (A) lying between 1.0 and 1.1. The second segment had A values between 2.1 and 2.2. Several other cells had A values of 6 to 7 for the second segment, while the A values of the other two segments

did not exceed 2. At liquid-nitrogen temperature the values of A increased drastically. For the first and third segments of the curve, A values ranged from 8 to 15, while the second segment had values of A between 17 and 33. Vavilov et al., in the other paper on silicon cells given at the conference (239), determined the value of A from dark I-V measurements. They obtained a value of $A = 1.0$ for zero bias and $1.0 < A < 1.4$ for a bias less than 100 mV. For bias values greater than 100 mV, A remained constant at approximately 1.4.

This paper also showed spectral response data on cells with junction depths of 2, 9, and 15 μm . This was apparently part of an attempt to optimize the junction depth. It was noted that the cells were made with an antireflection coating which was a natural result of the diffusion process rather than a separately deposited film. Removal of the film caused a decrease of about 21% in short-circuit current. The presence or absence of the antireflecting film had no appreciable effect on the surface recombination velocity according to the authors. The idea that the junction should be extremely close to the surface appears not to have been fully appreciated, since no cells were made with junctions less than 2 μm deep. Some data on solar cell performance under high illumination intensity were shown. The cell tested had an efficiency of 4.8% under normal earth solar intensity. This dropped to 2.1% at an intensity seven times the normal solar intensity. The temperature of the cells was maintained at 25°C for these measurements.

By 1958 the maximum observed efficiency of the silicon solar cell had increased to 14%. Unfortunately, the details of the work resulting in this increase do not appear in the literature of the time. A sales pamphlet written by N. J. Regnier of the Semiconductor Division of the Hoffman Electronics Corp. in April 1958 attributed the high efficiency to improved production techniques, some of which have been described above. The pamphlet gave information and specifications on a 5-W solar cell module developed by Hoffman for terrestrial use. Any number of the modules could be connected together to provide the required amount of power for a given application. The module consisted of 144 circular cells (approximately 1 in. diameter) mounted on an aluminum tray with a glass cover and was designed to deliver 5-W of power under an illumination of one Langley.

Prince and Wolf (193), also of Hoffman then, gave a figure of 14% for the maximum observed efficiency in a publication discussing silicon photovoltaic devices. Three types of photovoltaic devices were discussed: the photodiode, the solar cell, and the low-level solar cell. The general device characteristics were developed through the use of equivalent-circuit models. Some of the theoretical and experimental work necessary in designing the devices was also described. Three design considerations for the solar cell were discussed. These were reflection losses at the surface, generation of electron-hole pairs, and the diffusion and collection of the minority carriers (see section IV-A-3). Measurements indicated that the reflection losses of the cells (apparently without antireflection coatings) were well below 4% for most of the wavelength range of interest, and it was concluded that no significant improvement

could be expected in this direction. The fact that unity quantum efficiency exists for electron-photon interactions, determines the generation rate of minority carriers. The investigation of minority-carrier diffusion and collection led to several interesting results. First, it was concluded that most of the contribution of minority carriers came from the base or n-region in the long wavelength response. This confirmed the experimental finding that long minority-carrier lifetimes in the base were necessary for good collection efficiencies. Secondly, the need to make the p-layer as thin as possible was confirmed. Finally, the surface recombination velocity was found to have very little effect on the collection efficiency. Figure 51 is a silicon solar cell as shown by Prince and Wolf.

The low-level solar cell was designed specifically to operate at low light intensities (less than 1 foot-candle). The only important design change was a widening of the junction region. This was felt to be necessary to reduce the internal field emission, associated with narrow junctions, which lowered the impedance of the junction at small biases (low level illumination) and hence reduced the efficiency.

Some possible applications for the solar cell were also discussed in this paper. The applications fell into three categories. The first was as energy conversion devices

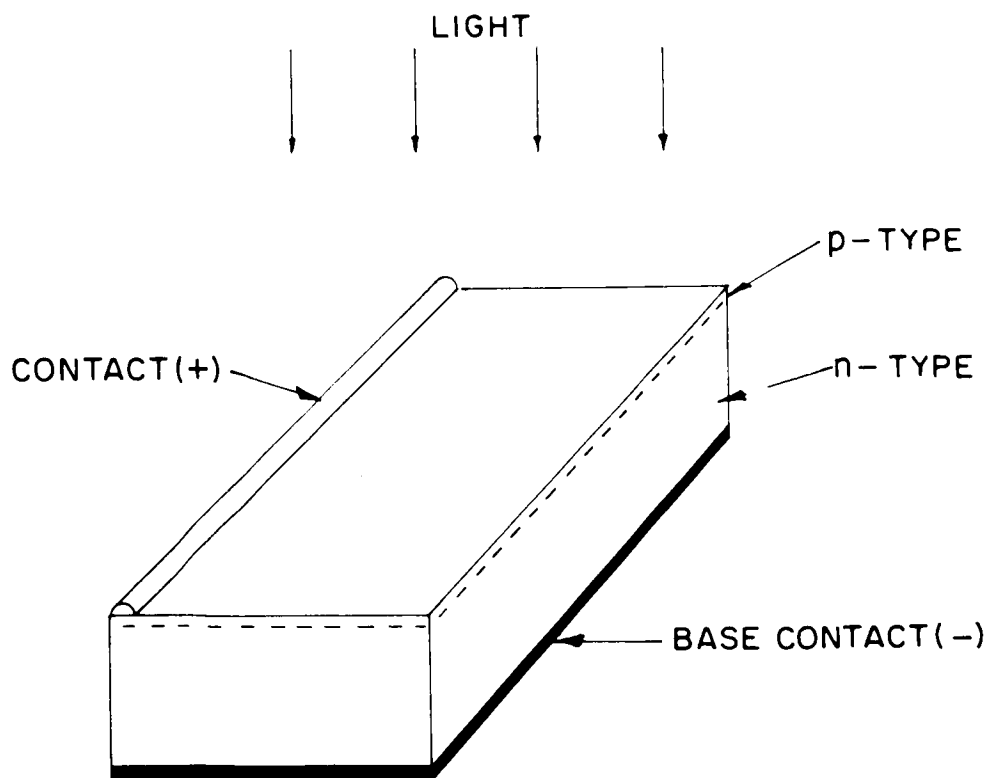


Figure 51. Silicon solar cell circa 1956, after Prince and Wolf.

like the 5-W module discussed above. The next application was that of a control device operating a relay or acting as the input for a transistor amplifier. The other suggested application was as a light meter, either linear or logarithmic depending on the loading condition.

The first space use of solar cells occurred in 1958 with the launching of Vanguard I on March 17. Vanguard used six panels of solar cells, each containing eighteen 2-cm x 1/2-cm cells as a secondary power source. The results of some tests which were designed to evaluate silicon solar cells for possible space use were given in a Lockheed Missile System Division report written by Brown et al. in June 1958 (240). Factors evaluated included spectral response, thermal effects, thermal shock, ageing, and the effects of meteorite puncture. The spectral response apparatus used was unique in that the light source used was the sun. A solar tracking system, mounted on the roof of the laboratory building, reflected a column of sunlight down a vertical shaft into the laboratory where it was focused onto the input of a monochromator. The cells tested (obtained from Hoffman) had an area of 2 cm² and an average efficiency of about 10%. The temperature dependence of the cell characteristics was as expected; however, 75% of the cells suffered severe permanent damage under the thermal shock test which consisted of immersion in liquid nitrogen. Meteorite puncture was simulated by drilling with a 0.12-in. -diameter diamond drill and by electric arc discharge. In general, a single puncture reduced the power output by 10 to 40%. Apparently the punctures resulted in shorting of the junctions.

In the same year Loferski and Rappaport published an experimental study of the effect of radiation damage on silicon solar cells (241). The study was intended to give an estimate of the lifetime of a solar power source on the International Geophysical Year earth satellite. The cells were irradiated with electrons, protons, alpha particles, X-rays, and ultraviolet radiation, the last two having no measurable effect. As a result of the tests, a drop of 25% in power output was estimated to require an exposure time, under the assumed conditions, of 10⁵ years. The assumed conditions were based on high altitude balloon data and are summarized in Table II. Loferski and Rappaport noted that there was a discrepancy of approximately 3×10^4 between the number of counts reported by geiger counters on the two 1958 I. G. Y. satellites and the number predicted by extrapolation from the balloon data. The right hand side of Table II shows the actual radiation sources used by Loferski and Rappaport in their experimental studies. The first reasonably accurate determination of the space radiation environment was then performed by Van Allen and others in 1959.

Rappaport (242) quoted a figure of 7 to 10% for the average efficiency of production silicon cells around 1958, depending on cell type and manufacturer. He estimated the future, quantity cost for a 1-kW solar cell power supply at \$200,000, the major cost being that of producing the single-crystal silicon wafers. The estimated weight of the power supply was 20 pounds. Much of Rappaport's discussion dealt with materials alternative to silicon.

TABLE II. COMPONENTS OF RADIATION IN THE UPPER ATMOSPHERE,
AND THE EXPERIMENTAL RADIATIONS SELECTED, AFTER
LOFERSKI AND RAPPAPORT

Upper Atmosphere			Experimental	
Radiation	Energy or Wavelength	Amount	Energy or Wavelength	Amount and Source
Ultraviolet	75 - 2200 Å 2200-3400 Å	6×10^{-4} mw/cm ² 4.8 mw/cm ²	2200-3400 Å	SH 9.8×10^{-3} w/cm ² S4 173×10^{-3} w/cm ² B-H6 2.1 w/cm ² UV Light Burners
X-Rays	7 - 60 Å	10^{-4} mw/cm ²	50 kev (0.24 Å) to 250 kev 0.75 to 2 mev	Up to 10 ⁴ Roentgens/hr X-ray Generator
Electrons (Auroral Regions)	10 - 500 kev	1%	2mev	Up to 100 μ a/cm ² Van De Graaff
Protons	≥ 1 B ev	80%	10 - 20 mev	Up to 100 μ a/cm ² Cyclotron
Alphas	Average in Nuclear Bursts 50 Mev	19%	40 mev	Up to 100 μ a/cm ² Cyclotron

No dramatic increase in efficiency was reported in 1959, although some improvements were made. Improvements in the growth techniques resulted in reduced frequency of dislocations and other imperfections in the silicon crystals as reported by H. J. Yearian of the Purdue Research Foundation (243). Working under a Signal Corps contract Yearian was able to reduce the dislocation density of grown silicon single crystals to less than 10 cm⁻². This was accomplished primarily by reducing the contamination of the gas flowing over the crucible in which the silicon was grown, by isolating the gas from the heater. This also resulted in a reduced occurrence of twinning.

The most important improvement occurring in 1959 was the introduction of an alloyed aluminum contact for the p-layer. By slow heating and cooling of the aluminum, a silicon-aluminum alloy was formed which gave a rectifying contact with n-type silicon and an intimate ohmic contact with the boron-diffused p-layer. The contact had a very low series resistance, resulting in an improved conversion efficiency (244). The same alloy, when formed by a fast heating and cooling cycle, formed a contact that was ohmic with respect to n-type material, with a contact resistance (0.1 to 0.2 Ohm for a 2-cm² area) comparable to that of the plated contacts of the time (245). The alloyed contact for the p-layer was developed by the International Rectifier Corporation under a Signal Corps contract. Very little of the solar cell research and development work during the middle and late 1950s was supported by the government, and the majority of the governmental support given during the late 1950s was supplied by the U. S. Army Signal Corps.

The two commercial suppliers of silicon solar cells in 1959 were Hoffman Electronics Corp. and International Rectifier Corp. J. Kalman of Hoffman published a summary of the characteristics of the commercially available silicon cells in early 1959 (246). This summary is reproduced in Table III. It should be noted, however, that much of this data was taken from sales literature published as early as 1956. A variety of cell sizes was offered, ranging from 1/8 cm² to 20 cm². The higher short-circuit current densities were near 30 mA. cm⁻², while the open-circuit voltages offered ranged from 0.48 to 0.58 V, with most of the Hoffman cells above 0.55. The efficiencies offered ranged from under 4% (reject cells) to greater than 12% for the 1/2 cm wide cells. The wider cells were series resistance limited, because no grid lines were used, and gave efficiencies only to approximately 11%. Recognition of this fact by Wolf at Hoffman in early 1959 led to an intensive search for practical production methods for the incorporation of grid lines into the cell structure. Die cut tape masks, stencil applied vinyl pre-polymer, and Kodak photoresists were experimented with, through which grid lines were formed by the electroless nickel plating process and built up by solder dipping.

The use of grid lines to reduce series resistance was adopted by all manufacturers in 1960, although acceptance by the users was somewhat slower. Various grid geometries resulted from the production techniques applied, as illustrated in Figure 52, with results in Figure 53. All of the major manufacturers reported improved efficiency due to this innovation (246, 247). Dale and Rudenberg of Transitron Electronic Corp. reported improving the average efficiency of laboratory-produced cells from 8-10% to 12-15%. This was accomplished through the introduction of an aluminum alloy grid structure to reduce the series resistance, and an application of a silicon monoxide antireflection coating to reduce reflection losses, which became necessary because of the different diffusion process used. These changes resulted in an increase of the maximum power voltage by 0.05 V, and reduced reflection losses to 2%. Although this experimental work was done at Transitron, commercial production of solar cells was not embarked on, and Hoffman and IRC remained alone in the market for cells. Investigators at Hoffman Electronics reported average efficiencies between 12% and 13% for experimental runs of gridded cells (249). International Rectifier Corp. introduced a

TABLE III. CHARACTERISTICS OF COMMERCIAL SILICON CELLS (1959) AFTER J. KALMAN

Manufacturer	Dimensions (cm)	Active Area (cm ²)	Output with Matched Load at 10,000 foot-candles		Avg. Conversion Efficiency (%)	Short-Circuit Current (mA)	Open-Circuit Voltage (mV)
			(mV)	(mA) (mW)			
Hoffman Electronics	2A	2.86 dia.	400	85 34	5-8.5 ^a	130	550
	200A	1/4 of 2A	400	21 8.4	5-8.5 ^a	32	550
	220C	2 x 2	400	65 26	5-8.5 ^a	100	550
	120C	1 x 2	400	34 13.6	> 9	40	550
	110C	1 x 1	400	17 6.8	5-8.5 ^a	20	550
	52C	0.5 x 2	400	15 6.0	5-8.5 ^a	20	550
	51C	0.5 x 1	400	7.5 3.0	5-8.5 ^a	10	550
	55C	0.5 x 0.5	400	3.8 1.5	5-8.5 ^a	5	550
	58C	0.5 x 0.25	400	1.8 0.72	5-8.5 ^a	3	550
	Intern'l Rectifier		Output with Incident ² Energy of 100 mW/cm ² (1 sun) ^b				
S1020 S1020A S1020B S0520 S0520A S0520B S0510 S0510A S0510B	1 x 2	1.75	350-400	17.5 7	4	35	480
	1 x 2	1.75	400	26 10.5	6	40	500
	1 x 2	1.75	400	35 14	8	48	550
	0.5 x 2	0.75	350-400	7.5 3	4	16	480
	0.5 x 2	0.75	400	11.2 4.5	6	18	500
	0.5 x 2	0.75	400	15 6	8	22	550
	0.5 x 1	0.37	350-400	3.8 1.5	4	8	480
	0.5 x 1	0.37	400	5.6 2.25	6	9	500
	0.5 x 1	0.37	400	7.5 3	8	11	550
(a) Average range.		(b) 10,000 foot-candles $\equiv 1 \text{ kW} \cdot \text{m}^{-2}$.					

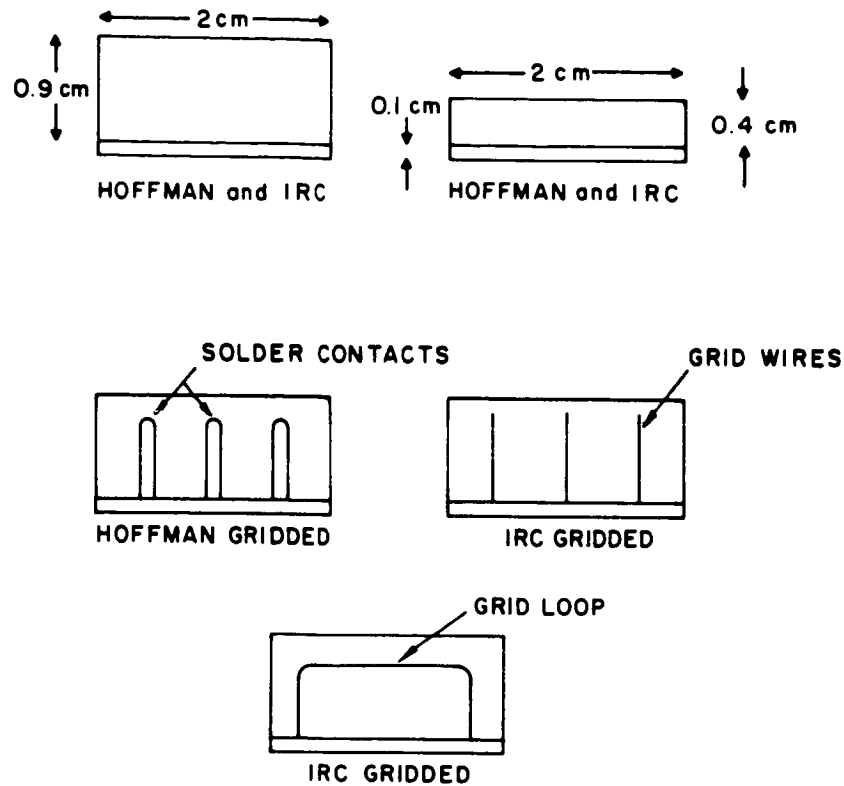


Figure 52. Cell types circa 1960

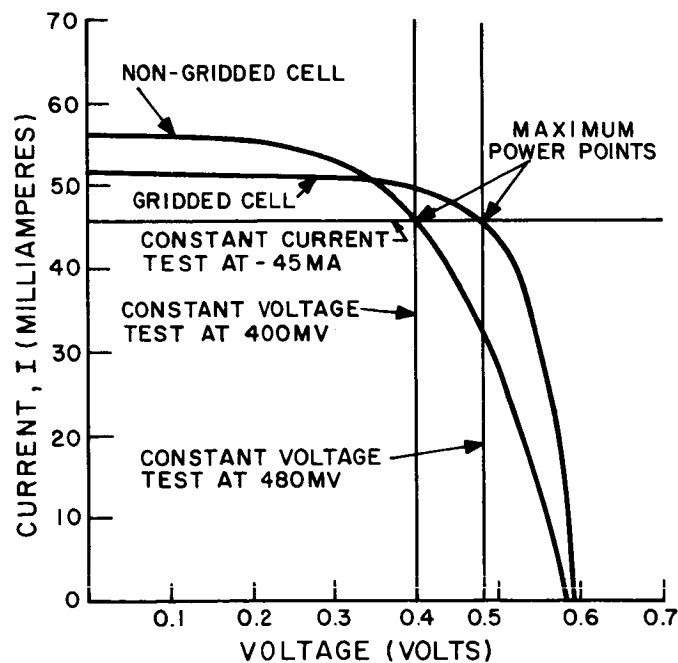


Figure 53. Current-voltage characteristics with maximum power points indicated and constant voltage and constant current test method for typical silicon solar cells, 1 x 2 cm size gridded and ungridded, taken at 25°C, after Wolf.

peripheral electroded cell as well as the grid line structure used by most other manufacturers (250, 251). The average efficiency of these production line cells was quoted as 10 to 12% with a maximum of 14%. Apparently as an advertising gimmick, International Rectifier produced a panel ("The Solar King") consisting of 10,640 cells having efficiencies of 4 to 5% and mounted it on the roof of an electric car (1912 Electromobile). The array was said to be capable of charging the car's batteries under "optimum conditions."

Reference (247) also provides a good survey of the general characteristics of the commercially available cells in 1960. Both Hoffman and I. R. C. are quoted as producing 13% efficient cells in quantity.

The use of optical coatings, both to reduce reflection losses and to control cell temperature, became a matter of increasing concern in 1960. As was mentioned earlier, a surface coating formed naturally during the diffusion of the junction of the p-on-n cells. This layer reduced reflection losses nearly perfectly. Dale and Rudenberg (248) pointed out the advantages of being able to control the diffusion process and the optical properties of the surface separately.

The Russians had also realized the benefits from antireflection coatings (252) for their n-on-p cells, although they did not use evaporated films. They settled on silicon dioxide as a coating because of its stability. After attempting a chemical deposition technique which left undesirable impurities on the surface of the silicon wafer, they decided on an oxidation of the silicon. Improvements of 20 to 25% in short-circuit current through the use of the silicon dioxide coating were reported. The details of the oxidation process were not given; however, the process was apparently thermal and hence not amenable to separate control of the optical properties and the diffusion process. No efficiencies were given for the cells used in these experiments.

The use of coated glasses and directly applied coatings to control cell temperature were discussed by Escoffery and Luft (253), but this had little bearing on the evolution of the silicon solar cell per se and will not be discussed in this section. The interest in cell temperature control had been stimulated by the use of solar cells in satellites, an application which also aroused interest in radiation damage.

A few authors published data on radiation damage in 1960. Dale and Rudenberg (248) reported that an integrated flux of 5×10^{13} 2-MeV electrons cm^{-2} lowered the efficiency of a silicon cell from 8.4% to 5.5%. The loss resulted primarily from a reduction of the base (n-type) minority-carrier lifetime from 3 μs to 0.02 μs . A more comprehensive set of data was given in Reference (247) which provided a summary of the findings of several investigators (Lockheed, G. E., S. T. L., and RCA). Table IV summarizes the high-energy particle densities in the Van Allen belts as recorded by various satellites (254) at the time. Table V summarizes the results of the investigations of several of the above companies.

TABLE IV. TYPE, ENERGIES, AND FLUX OF CHARGED PARTICLES

	Location	Energy	Flux
Electrons	Inner belt	> 20 keV	$10^9 \text{ cm}^{-2} \cdot \text{sec}^{-1} \text{ steradian}^{-1}$
	Inner belt	> 600 keV	$10^7 \text{ cm}^{-2} \cdot \text{sec}^{-1} \text{ steradian}^{-1}$
	Outer belt	> 20 keV	$10^{11} \text{ cm}^{-2} \cdot \text{sec}^{-1}$ "
	Outer belt	> 200 keV	$10^8 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ "
	Outer belt	> 2.5 MeV	$10^6 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ "
Protons	Inner belt	> 40 MeV	$10^4 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ "
	Outer belt	> 60 MeV	$10^2 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ "

TABLE V. EXPERIMENTAL DATA REDUCTION OF SOLAR CELL EFFICIENCY DUE TO PARTICLE BOMBARDMENT

Source	Particle	Energy (MeV)	Flux (particles cm^{-2})	Power Reduction (%)
Lockheed	Proton	3	5×10^9	25
		12	2×10^{11}	25
		12	10	50
STL	Electron	0.5	$2-8 \times 10^{13}$	25
RCA	Proton	17.6	10^{15}	50
	Electron	1.7	5×10^{14}	50
Transitron	Electron	2	5×10^{13}	35

An important conclusion of Table IV was that the lower-energy protons might possibly cause more damage to the solar cell than the high-energy protons.

The introduction of grid stripes removed the requirement that the diffused layer must be made thick to reduce series resistance losses. This allowed the separate optimization of junction depth to provide a better match to the solar spectrum. Several

experimental and theoretical studies of the variation of the spectral response of the cells with junction depth were published during the period 1960-1961 (255, 256). These studies showed that moving the junction closer to the surface improved the spectral response of the cell in the blue region and hence gave higher efficiencies, particularly in AMO sunlight. Cells with grid stripes and an optimized junction depth were expected to give a short-circuit current 10% higher than that of the ungridded cells under outer space sunlight conditions (256).

Another advance, originating around 1959, was an increase in the minority-carrier lifetime in the base region resulting in an increase in the long wavelength response (257). The increase in minority-carrier lifetime was a result of the availability of purer materials and improved crystal growing and diffusion techniques. The changes in lifetime in the base region initially caused some confusion in the measurement of cell efficiencies. The cells appeared to be more efficient than was actually the case, when tested under a tungsten light source, due to the great infrared content of the tungsten light. The combination of the grid contacts, improved base region lifetime, and optimized junction depth resulted in the considerable improvement in average cell efficiencies experienced in the period 1959-1961.

The improvements in cell efficiency resulted in a cost reduction on a dollars per watt basis. An additional improvement in cell cost during the period 1960-1961 resulted from a factor of two drop in the cost of silicon as reported by Prince (258) who gave a cost figure of 100 to 300 dollars per watt for cells in 1961.

The radiation damage suffered by cells exposed to Van Allen Belt radiation continued to be a matter of serious concern. Several government-sponsored projects at that time had as part of their mission the investigation of radiation effects and possible ways of reducing losses caused by them. An important development in this area occurred in mid-1960 with the discovery that n-on-p cells were considerably more radiation-resistant than p-on-n cells, by workers at the RCA Laboratories (259, 260).

Mandelkorn had then been experimenting with phosphorus diffused cells on p-type base material, exploring the potential advantages of the Russian approach and hoping for improved efficiencies. Some of these cells he provided to the RCA group for radiation effects evaluation, upon their request. The initial experiments showed that the n-on-p cells required 7.6 times as many particles (1.5-MeV protons) to produce a 25% decrease in efficiency as did a p-on-n cell of the same efficiency. Later investigations (261, 262) revealed a similar resistance to electron irradiation. There was some concern at the time that the n-on-p cells might be inherently less efficient than the p-on-n cells; however, this fear has proven groundless.

Several French publications on silicon solar cells appeared in 1961 (263-268). Most of these described laboratory studies intended to produce high-efficiency cells. Most of the French investigators had settled on the phosphorus-diffusion process (using P_2O_5) which to them appeared easier to operate and to give more reproducible results

than the boron trichloride process. It was also possible to get the high impurity concentrations necessary for reducing series resistance losses at much lower temperatures with the phosphorus diffusion process. This would aid in reducing the drop in minority carrier lifetime thought to result from the heating. The phosphorus diffusion resulted in a film being formed on the surface of the cell, the film being a phosphosilicate glass. This layer was etched away and reformed by oxidation several times until the short-circuit current was optimized. Efficiencies of 14% were reported. Salles (266) discussed some of the problems of carrying cell fabrication from a laboratory to a production process. Problems of matching and interconnecting cells for arrays were also discussed by Salles.

The status of solar cell development at Hoffman at the end of 1961 was summarized by Iles (269). Most cells were made from Czochralski-grown silicon with a resistivity around 1 Ohm cm. Grade IV (solar grade) silicon continued to be used since it had been reconfirmed that any potential gain obtained by using better grade material was found to be much less than the variations in quality introduced by the crystal-growing procedure. Different crystallographic orientations were again found to have little effect on cell output, although a change in crystallographic orientation frequently necessitated an adjustment of the diffusion procedure to yield equal results. (100) grown crystals were normally used because their shape gave less waste in cutting. The junctions were formed by the boron diffusion process and were, in general, less than 2 μm deep. Cells with junction depths greater than 1 μm were used only with a judiciously placed single top contact, while those with junction depths less than 1 μm used any of a variety of grid line configurations. Junction depths of 1/2 μm or less were actually the standard for space type cells at Heliotek; there was some difficulty in measuring such shallow junction depths because of surface roughness. The grid configurations included 3-line and 5-line patterns running parallel to either the short or the long dimension of the cell. Some of these had both main contacts on the bottom of the cell with the grid wrapping around the edge of the device.

Average resistivity of the diffused layer was 0.014 Ohm cm (15 to 25 Ohm square⁻¹) with a maximum surface impurity concentration of $5 \times 10^{20} \text{ cm}^{-3}$, resulting in a depletion region width near 0.03 μm . Base region minority-carrier lifetime for the cells was in the 3 to 10 μs range, while the diffused layer lifetimes were concluded to be of the order of 10^{-9} to 10^{-10} sec. Heating and cooling during the diffusion process was thought by the Hoffman workers to degrade the bulk minority-carrier lifetime by a factor of 2 to 3, which they felt to be tolerable. In contrast to this, the Heliotek workers had found the bulk lifetime data, obtained before junction formation, to be strongly influenced by trapping phenomena, and therefore unreliable. This applied especially to the larger lifetime values. On the other hand, it was found that cells prepared from material with only a few tenths of a microsecond lifetime would have base region minority lifetimes after diffusion in the normal 3 - 10 μs range. It was therefore concluded that the diffusion process had a gettering or annealing effect, especially since lifetimes in this range are among the highest reported for these resistivities.

At low values of current density the cells did not obey Shockley's diffusion theory or the space charge recombination theory of Sah et al. (see Section IV-A-1). The gettering effect experiments of Hooper and Queisser (270) in which glassy oxide layers were used to getter metallic impurities in silicon solar cells indicate that these materials were at least partially responsible for the anomalous behavior of the junctions. They suggested that the use of cleaner material might result in higher efficiency cells. Unfortunately, this was not borne out by experiment.

A good percentage of the experimental work during 1960-61 was aimed at lowering costs, reducing weight, and increasing cell area. Projects along these lines included work on dendritic cells, epitaxial silicon, cutting large wafers longitudinally out of the ingots, and preparing arrays of silicon spheres imbedded in plastic. These are discussed in detail later in this section. Work on efficiency improvement included studies of stacked cell assemblies and beam-splitting arrangements to break up the solar spectrum and direct the appropriate portions to cells with differing bandgaps. These are also discussed elsewhere. The efficiencies of the best cells were just below 15%. Clear-cut ideas for improving individual cell performance appear to be lacking although the work of Shockley and Queisser aroused some interest in the elimination of unwanted (i. e. , nonradiative) recombinations.

New developments in the field of radiation effects in 1961 included the discovery by Vavilov et al. (271) that lithium atoms interact with defects in silicon so as to neutralize a radiation-induced level. Tests were made on lithium-doped silicon samples which were irradiated with 0.9-MeV electrons. The samples contained considerable amounts of oxygen. Electrical measurements on the samples indicated that the $E_c - 0.17$ eV level introduced by the electron bombardment disappeared when they were heated to 330 to 350°K. The disappearance was accompanied by a sharp decrease in carrier density. Vavilov and his co-workers concluded that the lithium ions were freed from the oxygen bonds to move rapidly through the lattice at the higher temperature until they encountered a lattice defect where they tended to become localized. A localized ion would then capture an electron from the conduction band, thus neutralizing the site and causing a decrease in the carrier density. The idea that this type of interaction might provide a means of increasing the effective radiation resistance does not appear. A more detailed account of these and related experiments appeared the following year (1962) (272). At about this time some investigators at RCA, working under government contract, began to look into the possibility of producing radiation-resistant devices, including solar cells, through the use of lithium doping (273).

An interesting publication in 1963 by Smith et al. (274) described the design and fabrication of the power supply for the Telstar satellite. The Bell group decided to design and produce their own cells (through the Western Electric Co.) rather than buy them from commercial suppliers. The primary reason for this was a concern for the effects of Van Allen Belt radiation on the power supply. The superior radiation resistant qualities of n-on-p cells over p-on-n cells had just been found, and the need for higher radiation resistance was not yet generally recognized. Therefore,

n-on-p cells were not in production at the time that developmental work for Telstar was begun. Preliminary studies indicated that a suitable n-on-p cell could be nearly as economical in quantity fabrication as p-on-n cells of comparable initial performance in space and a developmental program was initiated late in 1960. The work was described in considerable detail by Smith et al. The final cell had the following characteristics:

Base material-p-type, 1 Ohm·cm, 15-mil-thick wafer, area 1 x 2 cm.

Contacts-5 grid lines + busbar, evaporated titanium silver with solder dip finish, width of grid 0.006 in.

Antireflection Coating - evaporated SiO₂, thickness - 800Å.

Efficiencies for a group of 10,000 cells ranged from 9.25% to 12.0% with an average of approximately 10.75%. The cells were designed to be sensitive in the blue-green region. No effort was made to obtain good long wavelength response (such as requiring high lifetime in the starting material) because the response in this region is primarily degraded by radiation. The paper gave a complete description of the assembly and testing of the power supply.

Developments in 1964 included work on wrap-around contact cells (275). A number of wrap-around contact cells were fabricated by workers at RCA and assembled into 10-cell modules similar to those used on Nimbus satellites. The cells had a 5% increase in active area over normal cells. The modules showed a 4% increase in power output over that of the Nimbus modules.

The status of solar cell manufacture in the United States as of early 1964 was summarized by V. Magee of the British firm of Ferranti Ltd. in a report covering his tour of American industry (276). The standard cell was a phosphorus-diffused n-on-p cell using either 10 Ohm·cm (for radiation resistance) or 1 to 3 Ohm·cm (higher voltage, and better load characteristic) base material depending on the power supply specification. Optimum junction depth was felt to be 0.3 to 0.5 μm by most manufacturers. All but one of the manufacturers checked used an evaporated layer of silicon monoxide (with a thickness of approximately 900Å) for an antireflection coating. The other manufacturer (Hoffman) applied the technique of using the phosphosilicate glass obtained in the diffusion process as the antireflection coating, a technique used by Ferranti also. There were two common approaches to the contacting problem. The first was based on the evaporation of two metals followed by sintering. In this process a thin layer (a few hundred Å) of either chromium or titanium was evaporated onto the silicon active surface. This was followed by a much thicker layer (1 to 2 μm) of silver. The surface was then sintered slightly above 600°C to improve contact strength and provide low resistance. The other approach was to deposit first an extremely thin layer of gold by chemical deposition and then deposit nickel over it by an electroless technique. Samples of production cells were obtained from both

Hoffman and Heliotek. These cells were believed to be representative of the best performance levels normally obtained in production by the American manufacturers at the time. The efficiencies of Hoffman's 1-Ohm. cm cells ranged from 10.7% to 10.9% while those of the 10-Ohm. cm cells were between 10.4% and 11.6%. Heliotek produced only 10-Ohm-cm cells at that time, and supplied samples with efficiencies of 11.2% to 11.4%.

Another report by Ferranti (277), published in 1965, discussed the status of British solar cell manufacture. The manufacturing procedures were essentially identical with those of most American manufacturers, as outlined above, with the exception of the application of the grid contact and the formation of the antireflection coating. The antireflection coating was formed simultaneously with the junction diffusion by oxidation of the surface as above. The grids were applied by a combination of chemical plating and photolithographic techniques. A layer of electroless nickel was first deposited on the surface of the silicon. This was built up with a layer of copper and finally a layer of gold to prevent tarnishing. No solder dipping techniques were used. The cells were comparable to those of American manufacturers and averaged around 10.5% efficiency for air mass zero (space) conditions. Cost figures for the British cells were given by Butcher et al. (277), also of Ferranti. The cost ranged from \$300,000 kW⁻¹ to \$110,000 kW⁻¹ for cell thicknesses between 10⁻² cm and 4 x 10⁻² cm, respectively. These figures correspond to weight-to-power ratios of 2.07 kg. kW⁻¹ and 7.4 kg. kW⁻¹. (The cost of American cells around the same period was about \$100,000 kW⁻¹.)

No major progress in silicon solar cell technology has been reported after approximately 1961. Refinement of production methods, and controls, have considerably improved yields and consequently average efficiency which now is close to the previously reported maximum. Production distribution now falls primarily into the 10.5 to 11.5% AMO efficiency range for 10 Ohm cm n/p cells, corresponding to 12.5 to 13.5% AM1. The improved yields were the primary reason for price reductions effected during this time. Considerable effort has been expended on radiation resistance and the reduction of cell weight during the 1960s. Thinner cells (220, 278), drift field cells (278), "blue shifted" cells (279), and dendritic cells were studied both theoretically and experimentally by various investigators along with numerous other innovations. This work was paralleled by the increasing developmental work on thin-film cells and compound semiconductor cells which had potential cost, weight, and radiation-resistance advantages.

3. A Brief History of Various Unsuccessful or Incomplete Attempts at Cell Improvement

a. *Cost Reduction:* The earliest attempts at effecting a large cost saving in the production of silicon solar cells were the attempts to introduce polycrystalline material. Like the workers at Hoffman, Russian investigators appear to have pursued this

approach as an alternative during the earliest phases of their work (236). The earliest polycrystalline cells had efficiencies which were an order of magnitude or more below those of the single-crystal cells of the time and therefore were felt to be not promising. Several years after the initial work the Russians reported much better efficiencies for the polycrystalline cells (280). Efficiencies of 4 to 8% (on an active area basis) were reported for cells measured under a solar intensity of 75 mW. cm^{-2} . The cells which had these efficiencies made use of a mesh-type grid contact to eliminate the resistance due to the grain boundaries. Approximately 30% of the total surface area of the cells was occupied by contacts. Gliberman et al. estimated that the use of polycrystalline material would reduce the cost of a solar cell power supply by a factor of 2 to 3.

A more recent evaluation of the possibilities of polycrystalline silicon for solar cells was given by Berman and Ralph (281). The cells produced in these experiments also made use of a mesh-type grid initially; however, tests indicated that the standard 5-line grid pattern used on single-crystal cells was also near the optimum for the polycrystalline cells. Both p-on-n and n-on-p polycrystalline cells were investigated. The spectral response of the p-on-n polycrystalline cells peaked at about $0.73 \mu\text{m}$ compared with about $0.85 \mu\text{m}$ for single-crystal cells. The shift to shorter wavelengths was attributed to a reduced minority-carrier diffusion length in the base region due to recombination centers associated with the grain boundaries. In general, the p/n polycrystalline cells were more efficient than the n/p polycrystalline cells. The best n/p cell efficiency as measured under sunlight ($\sim 100 \text{ mW. cm}^{-2}$ at Table Mountain, Calif.) was approximately 8%, while several p/n cells measured under the same conditions had efficiencies exceeding 11%.

The cost analysis of polycrystalline cell production indicated that further developmental work was necessary to improve the yields to the point where the cells would be competitive with single-crystal cells before any cost saving could be realized. The cost of single-crystal material (1964) was about \$0.40 per gram, while the cost of polycrystalline material was about \$0.11 per gram. The slightly higher breakage rate experienced with the polycrystalline material necessitated an adjustment in the average number of grams of material needed to produce a cell. This adjustment resulted in an average material cost per cell of \$0.80 for single crystal and \$0.28 for polycrystal. The manufacturing cost for both types of cell was estimated to be approximately \$2.30 per cell. When it was assumed that the yields for both types of cells were 100% (i.e., the efficiencies are high enough for all finished cells to be usable) a simple calculation showed that a 17% decrease in cost could be realized by using the polycrystalline material. This figure would apply in any case where identical yield distributions for the two types of cells could be achieved. Since this was not a realistic assumption, one had to assume some minimum acceptable efficiency for the cells and then make the comparison. When a minimum efficiency of 10% was assumed as usable, calculations showed that for the p/n configuration 80% of the polycrystalline cells would have to equal or exceed 10% efficiency in order for the cell cost to just equal that of the single-crystal cells (99% of single-crystal p/n cells were $> 10\%$). For

the n/p cells the breakeven point was a yield of 77% with efficiencies greater than or equal to 10%. The p/n polycrystalline cells averaged around 8 to 10% in efficiency and the n/p cells somewhat lower. No significant cost advantage could be expected until these efficiencies could be raised to the 10 to 11% range. This analysis was concerned only with reducing the material costs, since it was felt that any possible modifications of the cell manufacturing process which might produce further cost savings would be equally applicable to the single crystal cells.

One technique with potential for reducing production costs which has received considerable attention, is the use of larger area cells. The philosophy behind this approach is simply the reduction of handling costs per square cm of cell. A number of interesting ideas for the production of large-area cells have been explored. The most straight-forward approach is simply to grow larger (wider) silicon crystals. Cherry (282) reported the growth of crystals with diameters of 6 to 8 inches at Texas Instruments, normally used in the production of infrared optics. A wafer cut from such a crystal would have an area of 48 square inches. Not surprisingly, the breakage during handling of these wafers was extremely high. It was anticipated that special tooling might alleviate this; however, no further reports on single-crystal cells made from wafers of this area appear in the literature.

Similar approaches were experimented with at Hoffman Electronics Corp. in 1960, and were reported by Prince (283) and by Wolf (284). The techniques for the growth of crystals had been advanced by then to the point where crystals with a diameter over 2 inches were grown routinely in production, so that circular solar cells with areas of 3 square-inches could be fabricated, as well as cells with dimensions up to 2 cm x 7.5 cm, cut longitudinally from the ingots. Efficiencies greater than 12% were measured on some of these cells. When weighing the desirability of fabricating large area cells in this fashion, it must be remembered that the thickness of the diamond saw blades, and with it the cutting (kerf) losses, had to be increased with the depth of cut in the silicon. Solar cells are normally sliced from silicon blocks of 2 x 2 cm or 1 x 2 cm cross-section. This requires a cut of 1 or 2 cm in depth, and is now generally performed by internal diamond saw cutting methods or by stacked reciprocating blade and slurry methods, in both cases with the kerf losses well under 0.010 in. Deeper cuts require O. D. diamond blades with thickness near 0.020 in, or result in larger kerf with slurry cutting. Also, there will be a power loss due to series resistance even for an optimized grid pattern, although this can be minimized by increasing the thickness of the grids (at additional cost). Losses at interconnections are also more significant for larger area cells.

Some of the more original ideas for producing low-cost, large-area cells (including the 48-in.² cells above) were studied under government sponsorship. These included growth of epitaxial silicon films, recrystallization of evaporated silicon films, various techniques for producing sheets of silicon single crystal (282), and arrays of silicon spheres imbedded in plastic (283). Some of these are illustrated in Figure 54. The epitaxial growth process made use of the thermal decomposition of a silicon

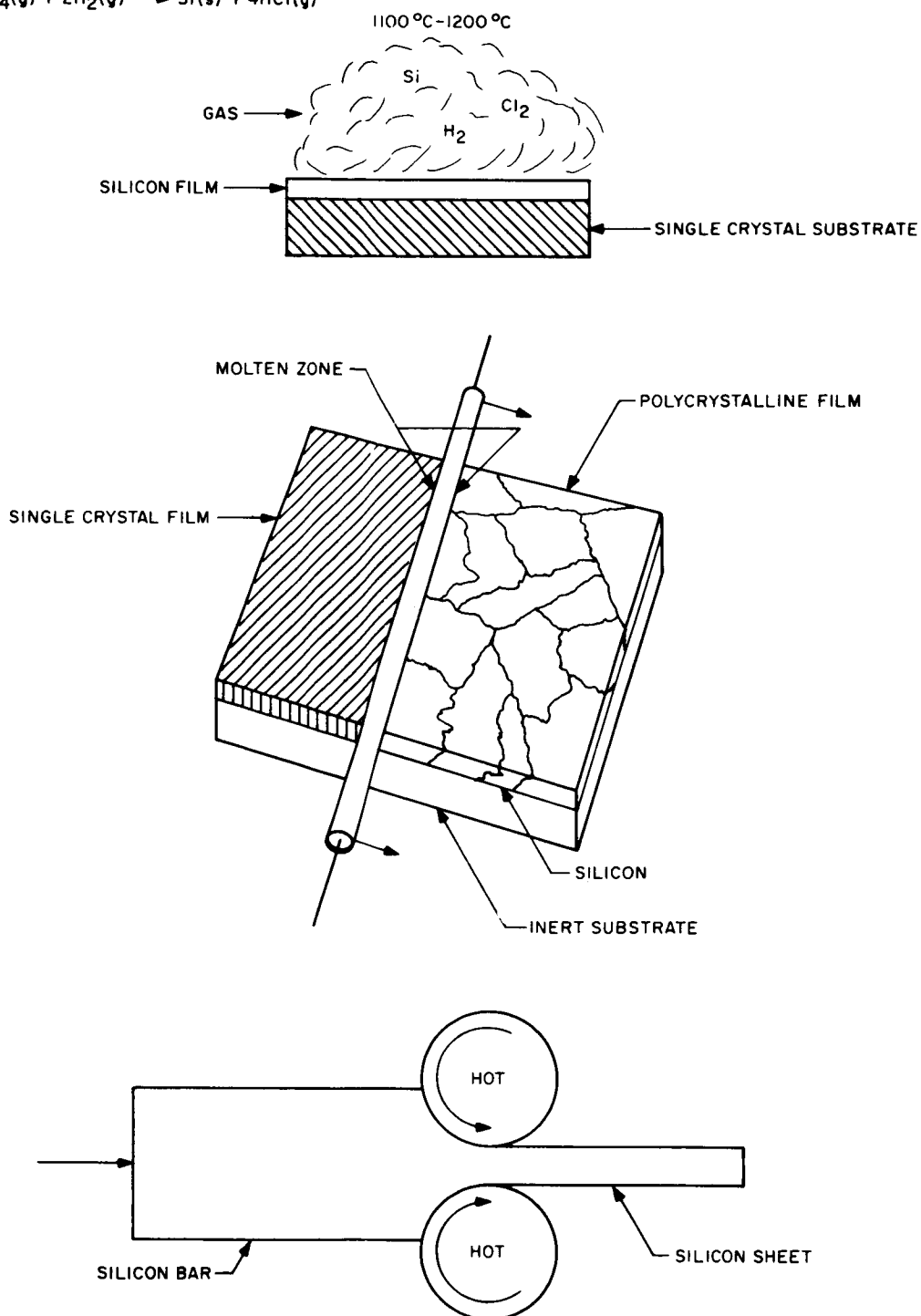
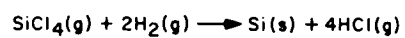


Figure 54. Large area silicon film formation, after W. Cherry, (a) epitaxial growth of silicon film, (b) recrystallization of evaporated silicon film, (c) rolling mill technique.

compound such as SiCl_4 to deposit a thin film of silicon onto an oriented single-crystal substrate. The substrate was intended to be of a material which could be peeled or dissolved away without damaging the silicon film. The original studies were performed using silicon substrates. It was also hoped that it might be possible to add the proper dopants during the growth of the film to produce a p-n junction, thereby eliminating another costly process. Epitaxial silicon techniques have been developed to the state where controllable and reproducible films can be grown on silicon and sapphire substrates today. However, it is doubtful that these techniques are the most economical for producing films of the proper thickness for acceptable efficiencies and of a realistic area (considering the fragility of large-area films). A proposed variation of the epitaxial process consisted of evaporating a suitable thickness of silicon onto a polycrystalline substrate, the substrate material being such that it would not be wetted by the silicon. The film was then to be recrystallized by passing a hot molten zone along it, and to be removed from the substrate. The degree of success achieved with this approach is not known.

A somewhat similar approach was suggested by W. Shockley (285). The technique consists of floating a layer or film of molten silicon on a molten metal. The silicon is then pulled across the frictionless liquid metal surface, by means of a silicon seed in the form of a thin sheet, through a temperature gradient to form a single crystal sheet. This approach was investigated by W. R. Grace & Co. under Signal Corps sponsorship (see above reference).

Thallium, lead, and bismuth were considered as supporting metals because they were felt to be suitably non-reactive and immiscible with molten silicon. Lead was finally chosen because of its slightly higher boiling point and the fact that it had a more limited effect on the electrical properties of silicon than the others. Several silicon wafers (2 inch dia.) were grown by this technique. All were polycrystalline with single crystal regions of several square millimeters.

It was found that the relatively high surface tension of molten silicon prevented the spreading of the silicon and would not allow the formation of a thin sheet under the existing conditions. The wafers that were grown were lens shaped with an equilibrium depth of 4 mm. This thickness was independent of the wafer diameter for diameters greater than 2 cm.

It was discovered that liquid silicon and lead were mutually soluble to about 3 atomic percent at temperatures close to the melting point of silicon, a fact which apparently could not be determined from existing data on the lead-silicon alloy system at the time. The Pb-Si system was studied by attempting to pull single crystal ingots of silicon from melts containing various amounts of lead. Silicon melts containing more than 5% lead yielded only polycrystalline ingots.

Attempts were made to pull a thin sheet of silicon from the molten lens using the thin sheet seed mentioned above. The dissolved silicon crystallized from the lead phase at the lower temperature surrounding the seed in sufficient quantity to interfere mechanically with the pulling. This disturbed the crystallization of the thin sheet from the molten lens. As a consequence this method could not be made to yield thin sheets in single crystal form and the effort was abandoned after one year.

In a program sponsored by the Air Force (286), Tyco Laboratories explored the possibility of depositing monocrystalline thin films on amorphous or micro-crystalline substrates using a solution growth technique. The technique was somewhat similar to the process used by W. R. Grace & Co. above in that the single crystal film was grown on the surface of a liquid metal. The technique, called the traveling solvent method (TSM), consisted of passing a solvent (metal) zone through a solid polycrystalline film under the influence of a temperature gradient. First a polycrystalline film of silicon was deposited on a molybdenum substrate using a halide transport type growth technique. A thin film of silver was then evaporated over the silicon layer. A suitable temperature gradient for moving the silver through the silicon film could be produced by heating the molybdenum substrate. The silicon would then dissolve in silver at the hot interface (Mo-Si) and precipitate at the cooler interface (Si-vacuum). By properly doping the silver it would be possible, in principle, to form a p-n junction during growth. Silicon single crystal platelets with areas of 2 mm^2 were observed to grow on the surface of a liquid bead of silver. A similar technique, using gallium instead of silver, was used to grow platelets of gallium arsenide, and the growth of cadmium sulfide crystals using a cadmium solution was also investigated.

The Signal Corps sponsored development work on an earlier invention by M. E. Paradise, of National Semiconductor Products, concerning a large area solar cell composed of silicon spheres (283). The silicon spheres were expected to be obtained ultimately from silicon saw dust, or droplets obtained in a shot tower, but were for the development program obtained by cutting single-crystal silicon into cubes, and tumbling them to make them spherical with a nominal diameter of 3 mm. After lapping and etching a p-layer ($\sim 3 \mu\text{m}$ deep) was formed on the surfaces of the spheres by boron diffusion. The spheres were then arranged in a hexagonal closely packed array on a plastic sheet and partially immersed in a semipolymerized plastic. The plastic was cured and a multilayered metallic film was deposited over the spheres and the plastic to provide contact to the p-layer. More plastic was used to cover the metal film, and the sheet was then lapped to expose a portion of the spheres. The exposed portions of the spheres were etched to remove the p-layer from this portion. More plastic was added until the spheres were completely submerged, with the primary intention of protecting the pn junction region. The surface of the unit was lapped, exposing only the n-type material. A metallic film was evaporated over the lapped surface, contacting the n-type material and providing a means for external contacting. A final insulating film of plastic completed the cell. The cell structure is illustrated in Figure 55. It was feared that a loss in light absorption would occur because of the reduced effective cell area caused by the gaps between the spheres. It was found,

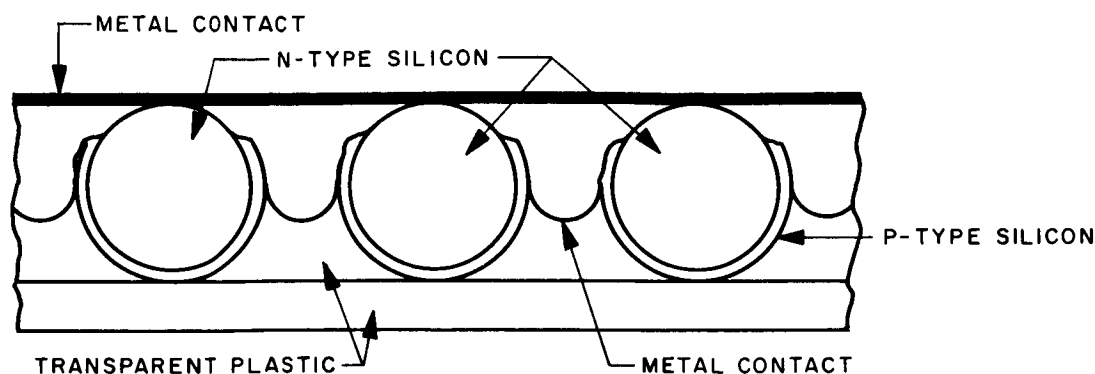


Figure 55. Flexible cell using silicon spheres.

however, that the structure resulted in a focusing effect due to the reflection from the silver coated plastic meniscus which formed one of the contacts. This increased the effective light gathering area considerably, and reduced the losses due to the spacing between spheres to a minimum. Efficiencies near 10% were measured on these cells; however, a cheap technique for producing the silicon spheres could not be developed. In addition, one would expect that the plastic used in this type of cell would be particularly vulnerable to both UV and particle radiation. An alternative approach using crushed silicon powder or chips yielded efficiencies of the order of 1%, non-uniformity of the individual components being a major difficulty. This last method has been used recently by some Philip's workers to produce cadmium sulfide solar cells.

Attempts have been made to produce silicon sheet by squeezing bars of silicon in a mandrel while subjecting them to high temperatures as in the rolling mill technique. Materials produced by this technique contained, not unexpectedly, a large number of strains and distortions. It was suggested that annealing might reduce these to the point where the material could be used in the fabrication of solar cells. This is questionable, especially considering the general effects of prolonged annealing on minority-carrier lifetime.

The most successful technique for producing silicon sheet has been the application of dendritic growth (285-293): see Table XVII in Appendix III. This technique begins by seeding two coplanar dendrites from a single seed. A silicon web freezes between the coplanar dendrites as they are pulled from the melt. The thickness of the web is controlled by the pull rate. Typical pulling speeds are 1/4 to 1-1/2 inches per minute. The thickness varies with pulling speed at a rate of about 30 mil/(inch per minute). The width of the web tends to increase as the growth proceeds. When the web is first seeded the edge dendrites are about 1/4 inch apart. They then separate, thus widening the silicon sheet, at a rate which is generally not constant but averages around 0.1 inch per foot of web pulled. The widening of the web can be quite erratic

and sometimes reverses. This obviously reflects the difficulties of controlling the growth process. The steady-state width of the web is a critical function of the temperature and temperature gradients around the dendrite tips under the melt surface. The temperature here must be controlled to within 0.02°C . Most grown web is 1 to 2 cm wide and 10 to 15 mils thick. Continuous lengths exceeding 8 feet have been grown. A section of such a crystal is shown in Figure 56. After growth the web is scribed to remove the dendrites and to provide a sheet of constant width. The dendrites and fillet regions, as well as the twin plane region, are areas of poor crystallinity. The sheets are then processed into cells using essentially the same techniques that are used in fabricating normal solar cells. Both p-n and n-p cells have been made with areas ranging from $1 \times 15 \text{ cm}^2$ to $1 \times 30 \text{ cm}^2$. Efficiencies as high as 13% have been reported for p-n cells (291) ($1 \times 15 \text{ cm}^2$). Most of the recent work has been on n-p cells. A pilot line run of this type of dendritic cell reported late in 1965 had the following yield characteristics ($1 \times 30\text{-cm}^2$ area cells) (284):

<u>Efficiency</u>	<u>Yield</u>
$\geq 9\%$	100%
$\geq 10\%$	68%
$\geq 11\%$	18%

Average efficiency for this run was 10.85% with a maximum of about 11.5%. The major difficulties with the dendritic cells are the requirement of maintaining uniformity over the length of the sheet and the handling problems associated with thin materials (294). The feasibility of the technique has certainly been established. It is difficult to make a cost comparison with conventional silicon cells on the basis of the information published up to this time.

In summary, the use of large-area cells offers potential savings in handling costs both for the cell manufacturer and the panel manufacturer. Historically, the solar cell size of $1 \times 2 \text{ cm}$ predominated until 1965. Since then, it has been replaced by the $2 \times 2 \text{ cm}$ cell, and it appears that the $2 \times 6 \text{ cm}$ is now achieving acceptance due to savings realized by its use. The dendritic technique has shown success in producing silicon sheet, but is not used in production. A number of the drawbacks of large-area cells, including breakage, etc., have been largely overcome. Additional factors to be evaluated when considering large-area cells for array fabrication are reliability, which may decrease when large-area cells are used, and the number of cells necessary to provide the desired voltage, which, for a fixed array size, may preclude the use of large-area cells.

Another approach which has been explored for possibly reducing production costs is the use of ion implantation techniques for junction formation (295, 296) see Table XVII. The junction is formed by bombarding the surface of the silicon with phosphorus ions with energies of 80 to 200 keV. An annealing step is necessary after bombardment. The annealing is intended to allow the implanted impurity atoms to take up substitutional positions and thus become electrically active. Typical annealing temperatures are 700 to 750°C with annealing times up to 16 hours. The junction depth is a function of the resistivity of the silicon material and the energy of the bombarding

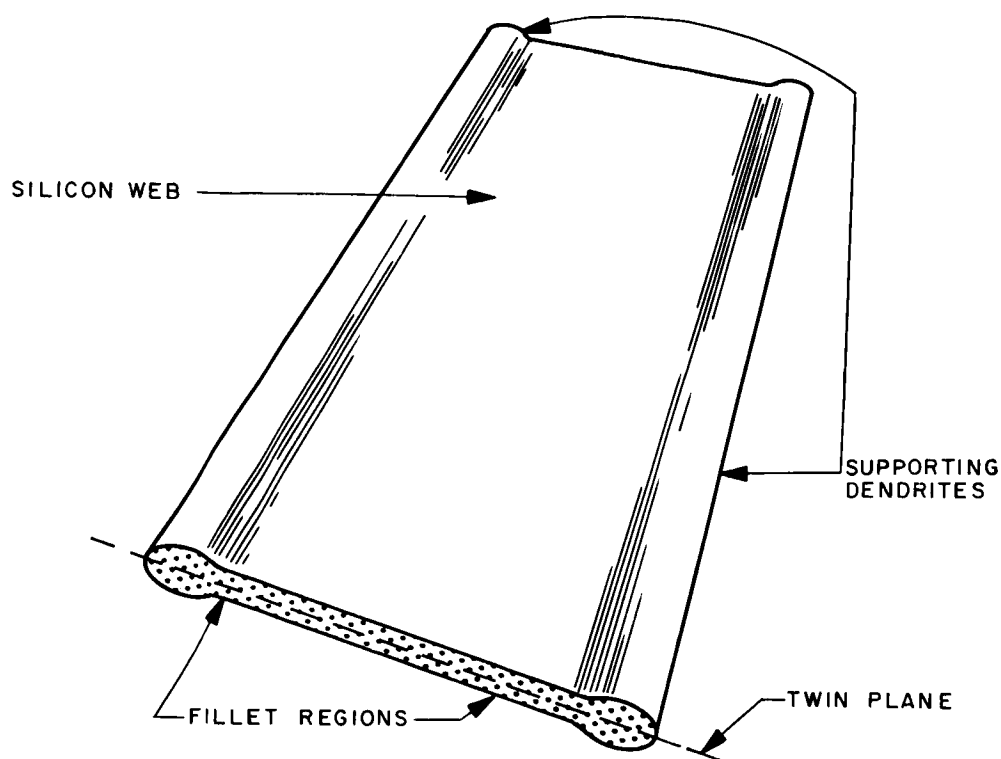


Figure 56. Section of dendritically grown silicon crystal.

ions. Extremely low energies (below about 70 keV) cause sputtering of the cell surface, increasing the surface recombination velocity. An energy of 80 keV gives a junction depth of about $0.4 \mu\text{m}$ in 10-Ohm-cm material. Single-crystal cells with efficiencies greater than 10% have been made by this technique with the major limitation being the resistance of the doped layer. This was expected to be overcome through use of ion implantation equipment with higher current capabilities. Recent trends (294) have been to combine the ion implantation process with the use of dendritic materials in an attempt to develop an automated process for producing low-cost solar cells with high power-to-weight ratios. Ion implanted dendritic cells with efficiencies of 9.4% (AMO) have been fabricated; however, serious handling and materials problems have prevented the setting up of a competitive production process.

b. Power-to-weight ratio: This has always been a matter of concern in the use of solar cells in space. Initially, the concern was generated by the low thrust capabilities of the rockets available at the time. Despite the current availability of high-thrust boosters, the demand for considerably higher power systems has caused a continuation of interest in increasing power density. There are basically two ways of accomplishing this: either increase cell efficiency or reduce cell weight. Increasing the air mass zero efficiency from the present 11% to 22% would essentially double the power density, assuming no major changes in cell structure are necessary to effect the increase. Achieving such an efficiency would necessitate the use of cells sufficiently thick to absorb essentially all of the photons with energies greater than band gap - a thickness of

more than 14-16 mils. Assuming 22% to be the practical upper limit to efficiency, an increase by approximately a factor of two in power density is the best that can be expected from this approach. In addition, the outlook towards major increases in cell efficiency has become less encouraging in recent years, although means for improving cell efficiency have constantly been sought.

Lately, a number of investigators have been studying the alternative technique of reducing cell weight by decreasing the thickness of the silicon wafer used. This approach incurs some penalty in overall efficiency but is the more logical approach because it offers potential power density increases greater than a factor of two and has the additional side benefit of providing a more radiation resistant cell. The loss in efficiency is primarily related to a drop in the short circuit current, but an unexplained drop in open circuit voltage also occurs. The loss in short circuit current is associated with two factors: the complete transmission of a portion of the long wavelength photons and the high surface recombination velocity at the back contact surface. These are two of the major problems associated with the thin silicon cells; another is the handling problem associated with the fragility of the thinner wafers. The 0.004" thick cell seems to be the practical limit for thin cells at the present stage of technology although data on cells as thin as 0.002" have been published.

The work of Wolf and Ralph (219) provided one of the first analytical studies of the special characteristics and problems of the thin cell. Their calculations showed that a 0.004" thick silicon cell would absorb approximately 84% of the available photons (compared with ~92% for a 0.016" thick wafer) under air mass zero sunlight irradiation. This gives a 9% loss in short circuit current density (and a corresponding loss in efficiency) from this factor alone. The experimental results of Wolf and Ralph did not agree with their theoretical predictions for cell thicknesses less than about 0.012". The data indicates a more rapid decrease in the effective minority carrier lifetime, as the thickness is reduced, than would be expected from the theory, which included the entire minority carrier generation, recombination, and collection mechanism. It was suggested by Wolf and Ralph that deeply penetrating surface damage might be reducing the effective thickness of the cell and thereby causing the deviation from the theoretical curves. A subsequent experiment in which they took precautions to eliminate work damage due to sandblasting was unsuccessful in confirming this idea. Paradoxically, Crabb and Treble achieved a much better agreement with the theory by "accurate measurement and the elimination of work damage at the rear silicon surface during fabrication of the cell". Their experimental curve shows considerably better agreement with this theoretical curve, but there is still an increasing deviation as cell thickness decreases. If the effective cell thickness were being changed by a constant amount (e.g. 0.002") due to work damage at the back surface it should be possible to fit the data to one of the theoretical curves by translating each data point along the cell thickness axis by this fixed amount. An inspection of the data indicates that such a procedure will in some cases improve the agreement somewhat but it will not totally eliminate the discrepancy. One is forced to conclude from this that either the effective thickness is changing by a nonconstant amount with cell thickness or that the effective diffusion length is changing more rapidly than would be predicted from considering the

effects of the proximity of the back contact to the junction. The work of Crabb and Treble indicates that the factor causing this degradation is probably some process parameter which may be controllable to some extent; although, again, they were unable to completely eliminate the effect. The work damage at the back surface is a contributing factor but is probably not the only cause.

The early calculations of Cheslow and Kaye of Electro-Optical Systems Inc. (297) indicated that one way to partially alleviate the effect of the high surface recombination velocity at the back contact of the thin cells is to incorporate a drift field into the base region. The purpose of this work (NASA sponsored) was to develop a radiation resistant solar cell, and a considerable amount of data, both theoretical and experimental, on 0.004" thick cells was obtained. A theoretical calculation indicated that an increase in excess of 20% in collection efficiency should result from the incorporation of a 40 V cm⁻¹ drift field into the base region of a 0.004" thick silicon cell, assuming a bulk lifetime of the order of 10⁻⁵ sec (see Figure 57). This analysis assumed the field, mobility, and lifetime to be constant throughout the base region. The experimental data presented by Cheslow and Kaye confirmed the prediction to some extent. Four mil cells with graded base regions had short circuit currents which averaged 6%-18% higher than those of similar cells without drift fields. Short circuit current densities for these 0.004" thick drift field cells ranged from 23.0 -28.5 mA cm⁻² under unfiltered 2800°K tungsten illumination simulating, apparently, AM1 conditions. These results are very encouraging but this approach to reducing the effect of surface recombination appears to have received no further attention in recent work on thin silicon cells. Further investigations in this direction might prove fruitful.

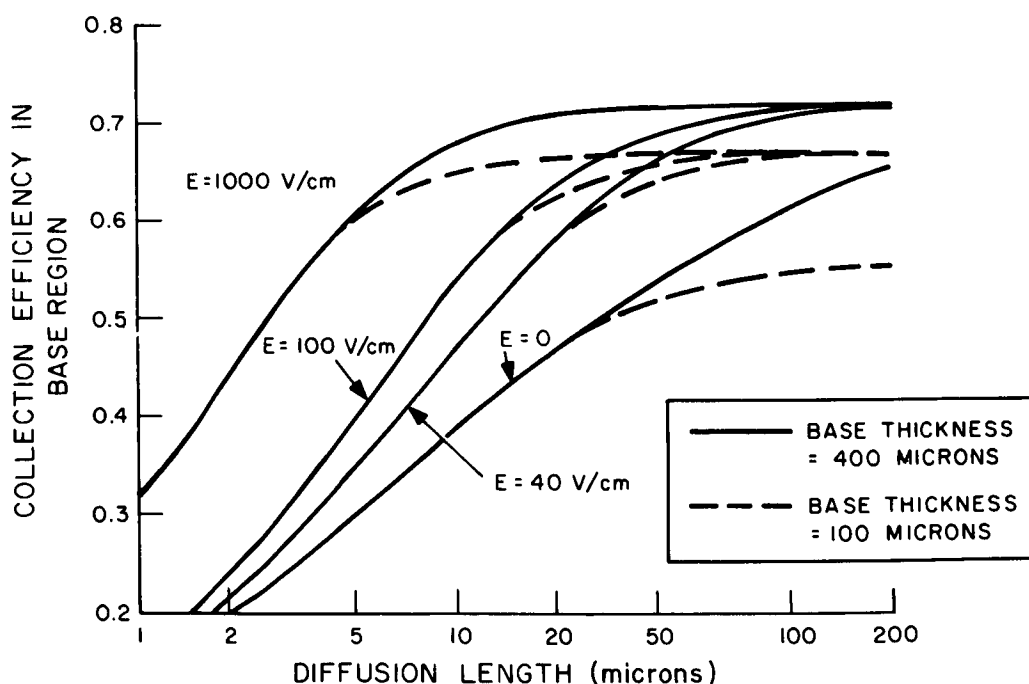


Figure 57. Collection efficiency for finite base as a function of electric field strength, after Cheslow and Kaye.

Another possibility for reducing surface recombination effects was serendipitously discovered in the course of the investigations of Burrill et al (294) into the use of optically reflecting back contacts for utilizing transmitted long wavelength radiation. The aluminum alloyed contact used to increase the reflectivity of the back contact was found to result in an increase in response over almost the whole spectral range below $1.2\ \mu\text{m}$. This was interpreted to mean that the surface recombination velocity at the contact had been reduced. Such an effect could, in principle, occur if the alloying of the aluminum contact resulted in a graded P^+ region adjacent to the contact. The graded P^+ region would reflect minority carriers away from the contact thereby reducing its effective recombination velocity. It is interesting to note, however, that data on the variation of short circuit current with thickness for reflecting contact cells whose back surfaces had not been polished prior to contact evaporation agrees quite well with the behavior predicted by the theory of Wolf and Ralph. A similar curve for cells with polished reflecting backs shows the more rapid drop off in short circuit current with thickness that was found experimentally by Wolf and Ralph, as does the curve for rough backed cells with a non-reflecting contact. This can be interpreted either to mean that the increase in short circuit current due to absorption of reflected radiation and lowering of the surface recombination velocity has almost exactly compensated the hyperdegradation of the current or that the source of the hyperdegradation has been eliminated in the case of the rough back reflecting cells. If the effect is mainly due to the absorption of reflected long wavelength radiation then the increases observed in cells under sunlight illumination will be considerably less than those indicated in (294) since these measurements were made under tungsten illumination which had a considerable percentage of its radiation in the wavelength interval between 1.0 and $1.2\ \mu\text{m}$. The reflecting contacts were originally conceived as a technique for reducing back contact heating and may prove useful where this is a matter of serious concern. Studies of the effects of these contacts on the performance of cells under sunlight illumination would be useful.

Ralph's paper (298) has provided the best summary of engineering data on thin silicon cells to date. In reducing cell thickness from $0.012''$ to $0.004''$ a drop of approximately 0.030 volts in the open circuit voltage occurred for cells made from both $10\ \text{ohm-cm}$ and $2\ \text{ohm-cm}$ material. From the data given, the drop is only partially explained by the drop in the short circuit current; the remainder being apparently due to a small change in the reverse saturation current (i.e., a factor of the order of $1.4 - 2.4$).

This change is consistent with a decrease in the effective lifetime in the base region of the thinner cells. An important fact pointed out by Ralph is that potential gains from the use of thin cells cannot be exploited until more advanced lightweight supporting structures (panels) and cover glasses have been developed. Some pertinent data regarding this is shown in Figure 58.

c. *Efficiency:* The theoretical maximum efficiency of the silicon solar cell according to the semi-empirical analysis of Loferski is 22% . The maximum efficiency observed on cells has been about 15% . No significant change in the maximum efficiency of experimental and production cells has occurred over the past seven years. There has,

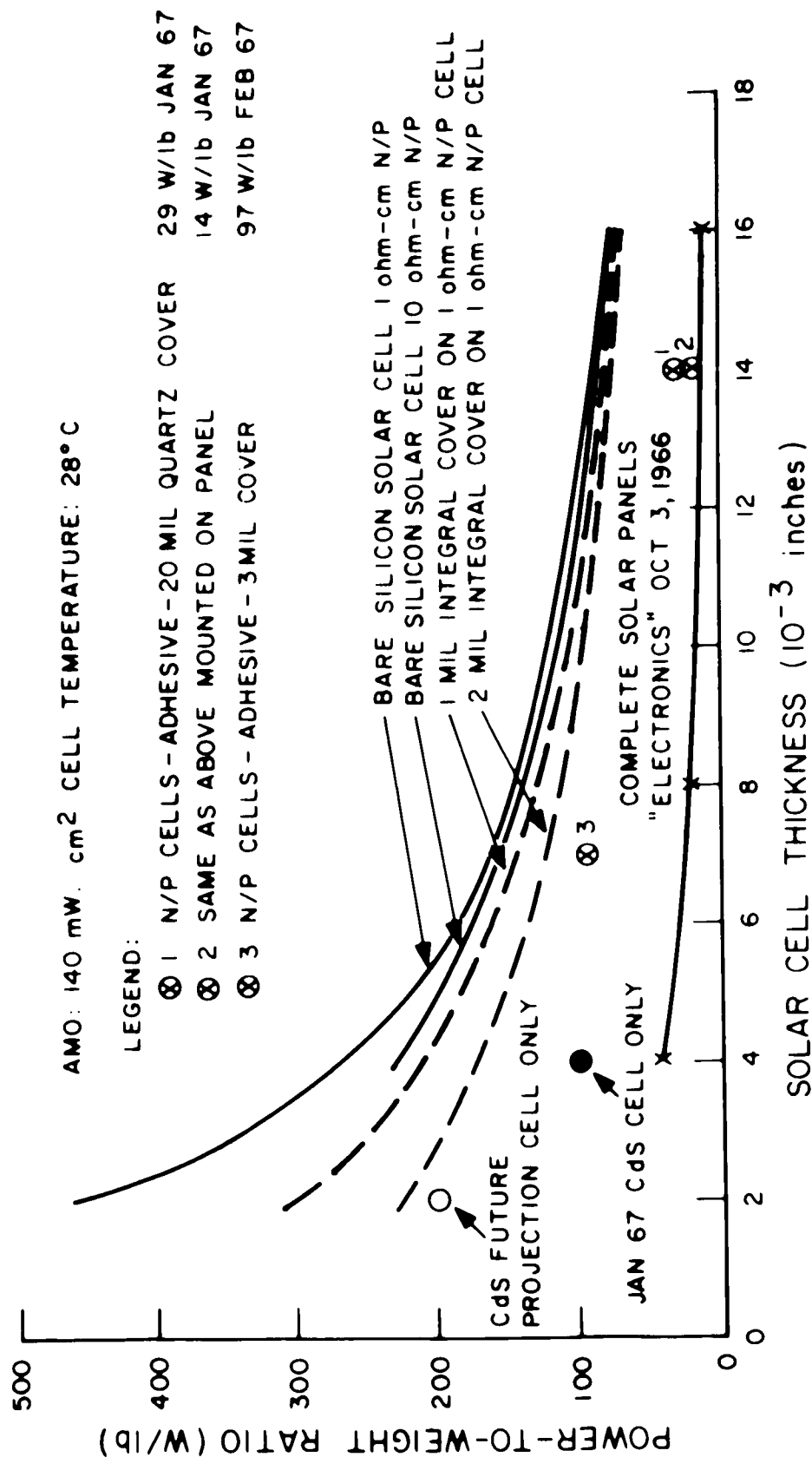


Figure 58. Solar cell power to weight ratio as a function of cell thickness, after Ralph.

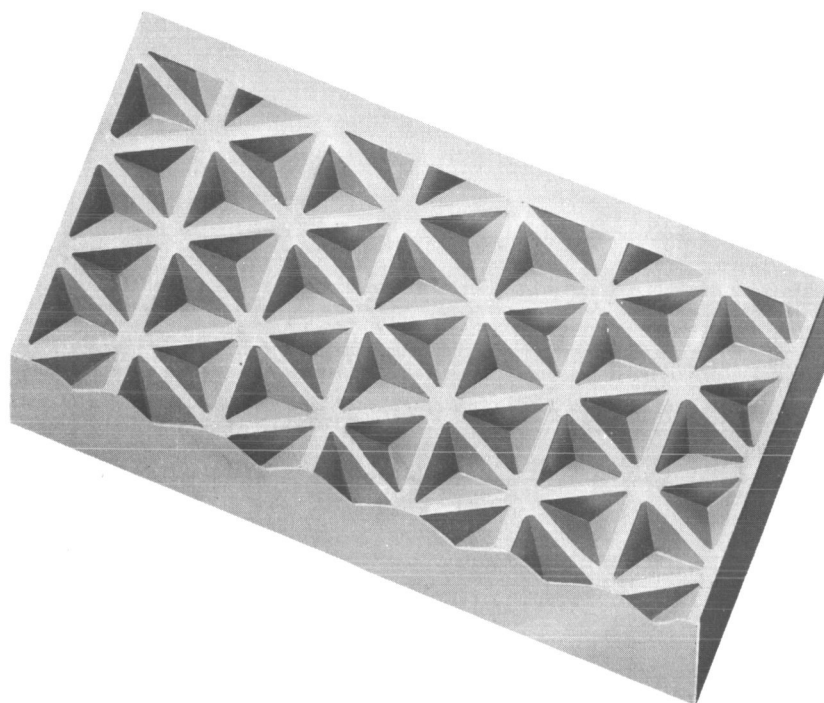


Figure 59. Tetrahedrally cut surface for antireflection effect.

however, been a gradual improvement in the average efficiency because of better materials, improved processing techniques, etc. ; so that the average moved closer to this maximum. Several ideas for obtaining radical increases in efficiency have been proposed since the introduction of the "Solar Battery". Many of these have dealt with materials other than silicon or combinations of two or more materials. These will be discussed in the later sections of this report. Others have not yet gone beyond the idea stage and have been discussed in section IV-A. There have also been some experimental attempts at improving silicon cell efficiencies (other than those which achieved success and have been discussed previously). Some of these experimental investigations will now be described.

The first loss which occurs is that due to reflection. Antireflection coatings have successfully reduced this loss to a minimum in contemporary cells; however, as a matter of historical interest, one other approach to solving this problem will be mentioned. In 1960 Dale and Rudenburg proposed an alternative approach to reducing reflection losses which consisted of cutting a pattern of inverted tetrahedral pits into the surface of the cell (248). The structure is illustrated in Figure 59. Each pit acted as a corner reflector so that incident light underwent three reflections before emerging. The structure was said to have a reflectivity of only 4% and had the advantage of being independent of wavelength. It did, however, result in a high series resistance. The technique would seem to be rather expensive and presents some formidable contacting problems. In addition, some degradation in cell characteristics

can be anticipated due to the increase in the effective area of the junction. This reduces the ratio of short circuit current density to saturation current density, thereby degrading the voltage and other dependent factors.

Efforts to improve absorption include the use of back contacts which reflect near infra-red radiation (299) and the use of fluorescent materials to convert a high energy photon to two or more photons of lower energy (300, 301). As was mentioned in the introduction, photons which are transmitted through the cell are usually absorbed in the back contact giving rise to heat which can degrade cell performance. If contacts, with suitable reflection properties when interfaced with silicon, could be devised some of these photons could be caused to pass through the cell a second time increasing the probability of absorption as well as reducing heating. This technique will not improve the efficiency of the conventional silicon cell significantly because it is sufficiently thick to absorb almost all of the photons capable of exciting hole-electron pairs. Thinner cells, however, might show measurable increases through the use of these contacts. Attempts to provide such a contact using an alloyed aluminum base were, at first, unsuccessful (299), primarily because of processing technology problems. Recent reports indicate that alloyed aluminum based contacts have been used successfully to increase reflection at the back surface of thin silicon cells (294). This work has been discussed in the preceding section on power-to-weight ratio.

Both Hoffman Electronics Corp. and Technical Operations Inc. investigated the possible use of fluorescent materials to convert high energy photons to multiple low energy photons. This technique has two potential advantages: firstly, lowering the photon energy means that it will be absorbed at a more favorable depth for collection; secondly, the creation of multiple low energy photons from a single high energy photon gives, in principle, a more efficient transformation of input energy to electrical energy.

Quite early in the development of solar cells (around 1956) the Hoffman Electronics Corporation investigated a number of materials for use in shifting the energies of photons (300). The earliest tried were a number of fluorescing dyes. With the exception of "Cerise Red Paint," all of these were found to degrade the performance of the cell even in the thinnest layers. When applied in thicknesses less than 0.003" the "Cerise Red Paint" neither degraded nor improved cell performance. When applied in thicker layers, performance was degraded in proportion to the thickness. This constancy of cell output for various thicknesses of the fluorescent dye was attributed to the balance between low energy photons lost through absorption in the dye and low energy photons created through the fluorescent process. Also to be considered is the fact that an amount of fluorescent light equal to that reaching the cell is emitted from the exposed phosphor surface. A number of phosphors consisting mainly of various proportions of cadmium sulfide and zinc sulfide with a variety of activators were tested. These also uniformly degraded the efficiency of the cells, dropping the power output by 10%-20% in the thinnest layers.

The work at Technical Operations Incorporated was sponsored by the Air Force Cambridge Research Center (301). This work explored the use of dye layers to convert both high and low energy photons directly to mobile carriers as well as the above

mentioned fluorescent technique. Fluorescent materials tested include acriflavin hydrochloride and a commercial cadmium sulfide green phosphor. Strongly absorbed monochromatic light was used to test the effectiveness of the fluorescent materials. Under this illumination no power output could be detected from the cells, even in the microampere range, for any of the materials. The minimum input power to drive a bare cell was found to be approximately 0.01 mW cm^{-2} (this gave a current of 20 microamperes). The intensity of the monochromatic illumination was found to be 0.1 mW cm^{-2} . The fluorescent illumination, while visible to the eye, was considerably less than 0.01 mW cm^{-2} and hence was not capable of generating a current in the cell which would have been measurable in the circuit used.

The idea of using dye layers to convert photons in the range $0.30\text{--}0.45 \mu\text{m}$ to hole-electron pairs was ill conceived since the problem is really one of collection rather than absorption. Acridine yellow and silver bromide layers were used in these experiments in hopes that they would "sensitize" the cells by absorbing high energy photons and transferring this energy to the silicon by carrier emission or vibrational coupling. Needless to say this approach was completely unsuccessful as was a similar approach for converting low energy photons ($>1 \mu\text{m}$) to carriers. In this latter case the dyes used (pinacyanol and other photographic dyes) would in fact increase the absorption of long wavelength photons but the carriers created must appear near the surface of the diffused region of the cell. This, as with the high energy photon case, makes their collection by the junction extremely unlikely.

Another approach to reducing series resistance losses (other than the use of grid lines) was to coat the cells with a transparent conductive coating. This was investigated by the RCA group at Mountaintop, Pa. (299). The coating was used in conjunction with the conventional grid stripes. Two coatings were tested, tin oxide and gold-impregnated silicon monoxide. Neither coating improved cell efficiency, and investigations in this direction were quickly abandoned.

Ralph and Biekofsky (249) attempted to obtain higher efficiency cells through the use of higher purity silicon. High purity (Grade I) silicon was substituted for the less expensive "solar grade" material in cell fabrication. A comparison of 32 cells made with grade I material and 32 control cells made with solar grade material indicated that the control cells were superior. The average efficiency for the 32 control cells was 12.7%, while that of the high purity cells was 11.1%. Mean characteristics were as follows: control cells - V_{oc} 0.585V, I_{sc} 56.0 mA; high purity cells - V_{oc} 0.565V, I_{sc} 54.5 mA. It was found, upon later measurement, that the bulk lifetime of the high purity material was somewhat lower than expected, indicating possible contamination.

d. *Radiation Resistance:* Proposals for increasing collection efficiencies included the use of drift fields. The first speculation about the effects of drift fields in solar cells occurred in the late nineteen fifties (194). The effects of drift fields on minority carrier

transport in semiconductors had been treated in the middle nineteen fifties (302, 303) in some of the early analyses of frequency response and transient effects in diodes and transistors, but none of this was applied to photovoltaic devices until the early nineteen sixties. A discussion of the theoretical studies of the effects of drift fields on solar cells, which began around 1960, is given in Section IV-A-5 of this report. Another development in 1960 was the suggestion by W. V. Wright that a drift field in the base region of the solar cell might improve its resistance to the effects of radiation damage (234). In the following year Electro-Optical Systems Inc. began a feasibility study under NASA sponsorship to develop graded base silicon solar cells with the primary aim of reducing the effects of high energy particle bombardment on efficiency (297). In the experimental portion of the study both n-on-p and p-on-n graded base cells were produced and tested. The graded base cells were produced by diffusing boron (in the n-on-p case) into a wafer of 25 Ohm.cm silicon material. Relatively long diffusion times and high temperatures (as compared with junction formation) were used in this step. Typical impurity gradients in the cells are shown in Figure 60. The initial graded base cells were found to be not significantly different from ungraded control cells because the graded region extended only to within 25 microns of the junction, leaving a 25 micron field free region adjacent to the junction. Extending the graded region to the junction yielded cells which, while showing no initial efficiency advantage over commercially available cells (maximum efficiency 11%), were 3 to 20 times more resistant to electron

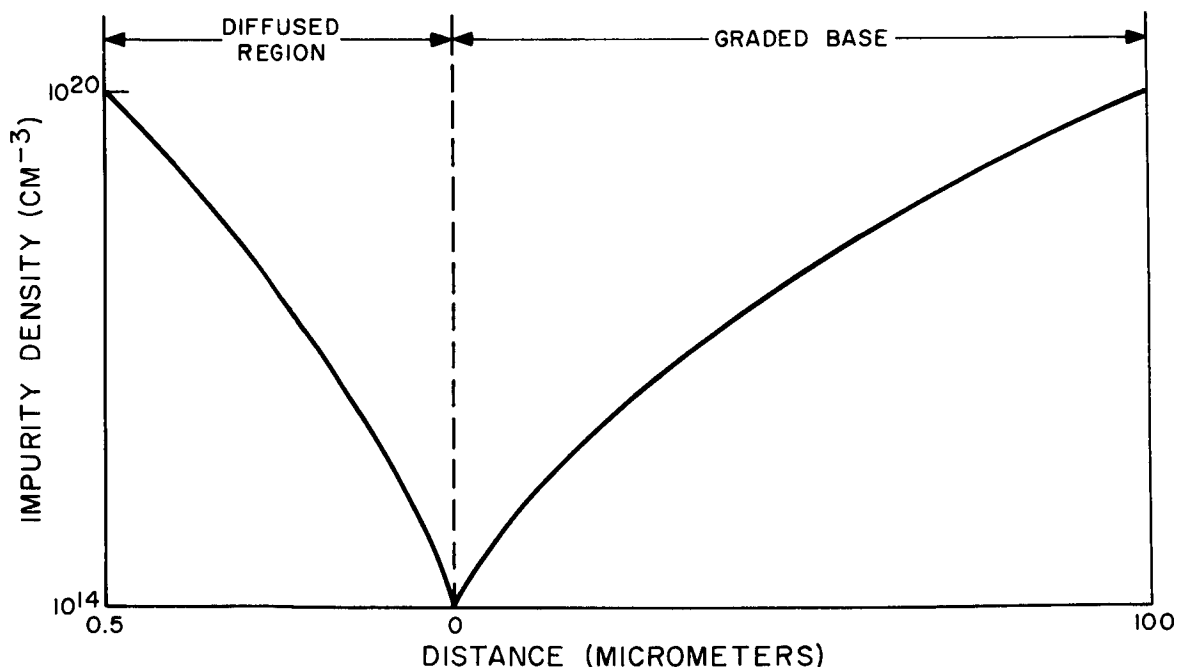


Figure 60. Typical impurity gradients for drift field cell.

and proton damage. It was noted that 4 mil thick cells with drift fields had almost 20% higher short circuit currents than field free cells. Tests indicated that in several cases the control cells also showed superior radiation resistance to commercially available cells although falling somewhat below the drift field cells.

Early in 1964 Electro-Optical Systems began working on the fabrication of epitaxially grown drift field cells (304). In the formation of these cells boron was deposited on the surface of a high resistivity silicon blank and diffused to a depth of 55-60 microns. A 125-150 micron thick layer of low resistivity silicon was then epitaxially deposited on top of the resulting drift field region. The cell was then lapped, etched, and phosphorus diffused to form the junction. The cell was completed by applying grids and an anti-reflection coating. Cells with efficiencies as high as 9.6% were fabricated during the first half of 1964 by this technique.

Texas Instruments Inc. and Heliotek also began experimenting with the use of drift field cells to improve radiation resistance in 1963. Both companies were sponsored by NASA in this work (305, 306) and both used epitaxial techniques. Texas Instruments explored the possibility of producing a resistivity gradient by programmed doping during the epitaxial growth process. This was an ideal technique because it eliminated long diffusion cycles, however, it apparently was not developed to a practical stage. The majority of the drift field cells made at Texas Instruments were made by depositing a high resistivity epitaxial silicon layer onto a heavily doped silicon blank and diffusing the impurities from the heavily doped silicon into the epitaxial film to give a resistivity gradient. A junction was then formed by diffusing phosphorus into the front of the cell. Cells with efficiencies as high as 9.7% were made in this manner (307). Surface layer gettering techniques were used to improve carrier lifetimes in the materials after the epitaxial deposition. Some of the drift field cells produced by Heliotek utilized an evaporated sintered silver-titanium back contact. These cells were generally more efficient than those using the conventional electroless nickel deposition process. Heliotek reported efficiencies in excess of 10% for some of their drift field cells.

Westinghouse Electric Corp. has investigated the possibility of developing drift field cells using dendritic silicon (290). Both epitaxially graded and diffusion graded cells were fabricated. The epitaxially graded cells had generally higher efficiencies than the diffused cells and were comparable in radiation resistance. An attempt to produce drift field cells by out-diffusion resulted in cells with very low efficiencies. The efficiencies of all of these drift field solar cells fell well below those of normal commercial silicon cells. The maximum for the epitaxially graded cells was 11.5% and for diffusion graded cells 8%. A study of the correlation between radiation resistance and drift field width indicated that the optimum width lies between 30 and 40

microns. The cells showed a superior radiation resistance to fluxes of 1 MeV electrons when compared with commercial N/P cells (10 Ohm.cm and 4 Ohm.cm) but the results of bombardment with other particles and at other energies were inconclusive.

The most recent analysis of drift field cells was performed by Kaye and Rolik (see discussion in Section IV-A-5). They determined that, for lifetimes corresponding to damage caused by a total flux of 10^{16} 1 MeV electrons, the optimum drift field thickness (yielding maximum collection efficiency) lies between 50 and 100 microns. Experimental cells having near-optimum drift fields were constructed for testing and comparison with cells having non-optimum drift fields and field free cells. The results of their experimental work are shown in Figure 61. The near-optimum field cell is indeed superior to the other two at the specified integrated flux level, although not grossly so. The near optimum cell also shows slightly better radiation resistance at the lower flux levels, but its initial short circuit current is lower than either of the others. The non-optimum cell for which data is shown had a drift field region thickness which was smaller than the optimum. Comparison with a cell having a field considerably wider than the optimum (e.g. 150 μm) would also have been interesting.

The most important recent development in solar cells has been the development of the lithium-diffused radiation-resistant cell. Work on this originated in 1962 and has been supported by a number of NASA contracts (308-310); see also Table XVIII in

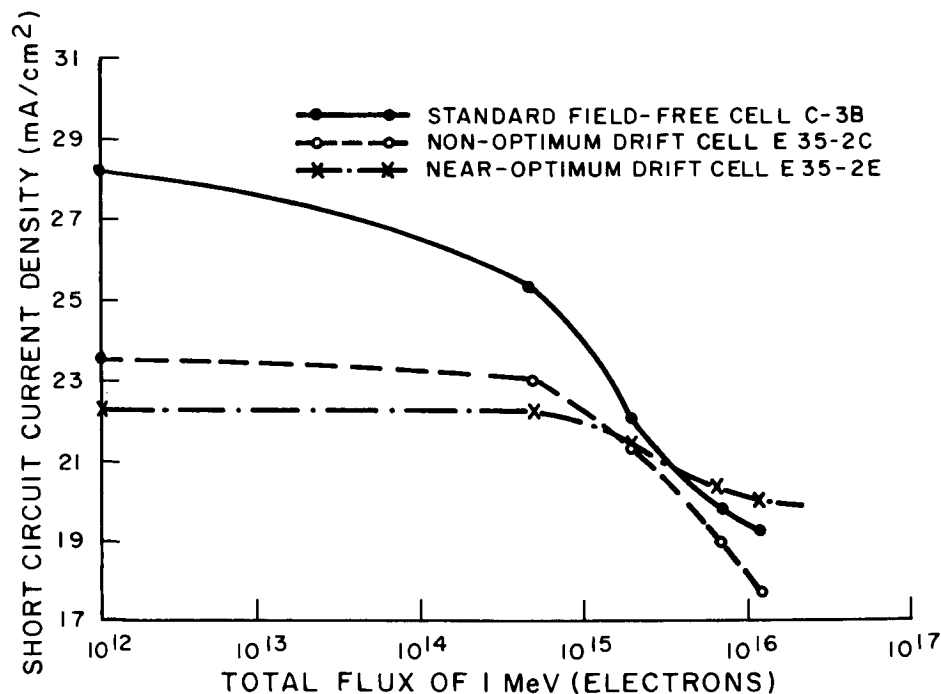


Figure 61. Short-circuit current density as a function of integrated 1-MeV electron flux for three types of cells, after Kaye and Rolik.

Appendix III. The cells have been shown to have a definite ability to recover from radiation damage (311). There still exists, however, a lack of understanding of the mechanism of introduction of the defects in lithium-doped silicon, and of the annealing process. Figure 62 shows a control cell made from the same silicon material as the lithium-doped cell under 1-MeV electron bombardment. Irradiation was stopped periodically and the cells were allowed to anneal at room temperature for the times indicated. The presently dominating view is that the recombination center is the result of a pairing between a radiation induced vacancy and a lithium ion. The recovery mechanism then involves the diffusion of another lithium ion to the recombination center, and its pairing with the lithium-defect complex.

It has been established that the speed and extent of recovery are strongly dependent on the amount of free or unpaired lithium. This factor has been particularly apparent in studies of the differences in annealing rates between cells made from silicon grown by the quartz crucible technique and that produced by the floating zone technique. The float-zone material has a considerably lower oxygen content than the quartz crucible material. Lithium interacts with many types of impurities and defects and, in the case of oxygen, forms stable LiO^+ pairs. If oxygen is present in appreciable amounts the ability of the lithium to diffuse to a damage site will be considerably inhibited and annealing times can become quite lengthy at normal temperatures. Annealing rates in some samples of quartz crucible silicon were so slow that early investigators concluded that annealing by Li did not occur in this particular type of material. It is apparent that in order for lithium to provide relatively fast recovery for radiation damaged solar cells it is necessary that the cells be made from silicon which is relatively free of oxygen.

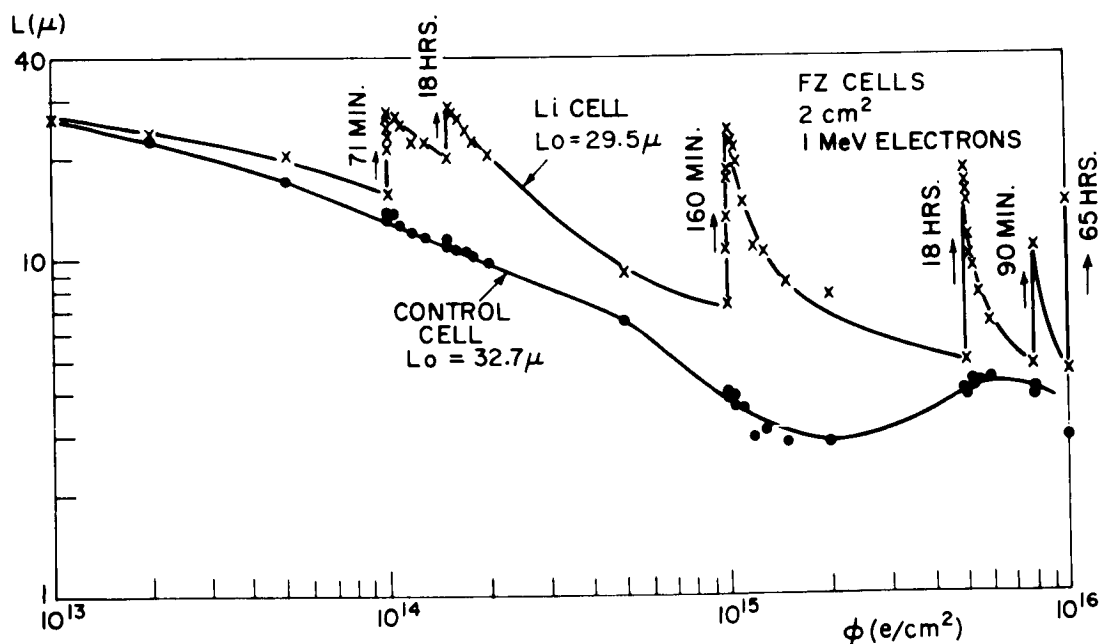


Figure 62. Comparison of the performance of n/p and Li-doped silicon cells under irradiation.

There is some evidence that a cell structure which incorporates a diffused phosphorus layer next to the junction (i. e., between lithium-diffused region and p-region) to give a three-layered p/n(P)/n(Li) structure, provides a device with improved radiation resistance without sacrificing the ability to recover. While high-efficiency (13 to 14%) lithium doped cells have been produced, the lithium-doped cells, on the average, appear to have lower efficiencies than comparable cells without lithium doping. The properties and possibilities of the lithium cells are receiving considerable attention at this time.

e. Metal-silicon and oxide-silicon interfaces: After a few early experiments with gold-silicon barriers on solar cells had been carried out by Ralph and Wolf at Hoffman Electronics Corp. in 1959, with low open-circuit voltages, short-circuit currents, and hence efficiencies of less than 5%, being obtained, the photovoltaic characteristics of metal-silicon interfaces were studied in more detail at Tyco Laboratories under Air Force sponsorship (AF19(628)-2845; see Table XVI in Appendix III) in conjunction with surface states studies (286). Both gold-silicon and aluminum-silicon contacts were investigated. Gold on n-type silicon and aluminum on p-type silicon were the most sensitive combinations, yielding maximum efficiencies of 2% and 3.5% respectively.

The devices were made by evaporating a transparent film of one of the above metals on the freshly etched surface of a circular silicon wafer. A peripheral electrode was deposited to act as a current collecting electrode. The opposite side of the wafer was nickel plated to provide a large area ohmic contact. The optimum metal film thickness (i. e. the thickness which resulted in highest photo-current) had a transmission of 27% for tungsten light. This figure precluded any expectation of a high efficiency device. This limitation could have been overcome by the use of grid lines, however, the purpose of this work appears to have been the investigation of the effects of surface oxide layers and surface states on the photovoltaic characteristics of the metal-semiconductor interface rather than the development of a device.

The effects of the oxide layer thickness on the properties of the Au-Si device were investigated by exposing a dozen wafers from the same ingot to a thermal oxidation treatment (550°C) for different time intervals. The varying oxide thickness was found to have little effect on the open circuit voltage, however, the short circuit current exhibited a rapid initial decrease followed by a more gradual decrease as the grown oxide thickness increased beyond 5Å. The data indicate that the thickness of the intrinsic (i. e. naturally occurring) oxide layer is approximately 7Å.

The Fermi level at the semiconductor surface as a function of temperature (100°K-400°K) was studied by the use of capacitance and open circuit voltage measurements. The temperature variation of the Fermi level position and the photovoltaic characteristics indicates that there are two surface states located at positions 0.3 eV and 0.52 eV below the conduction band. These states were found to have a profound effect on both the open circuit voltage and the short circuit current. The surface states appear to contribute to charge separation in a manner which is not well understood.

C. COMPOUND SEMICONDUCTOR CELLS

As noted in Section III-C, the success of the early silicon cells was closely followed by work on compound semiconductor cells by Gremmelmaier (GaAs), Talley and Enright (InAs), Reynolds (CdS), and Avery et al. (InSb). In this section, the progress in this field of research will be followed from 1955 to the present day. However, work on thin-film cells (which have been based almost exclusively on compound semiconductors) will be described later. In an effort to provide maximum continuity, an account will be given of the development of cells based on each compound for the entire period 1955 to the present. Thus, the following account is not in overall chronological order. Where connections exist in the development of cells of different materials, suitable indications have been given in the text.

Much of the support for research and development in this area has come from government agencies; see Table XIX in Appendix III for a summary of these.

In general, the choice of semiconductors for investigations aimed at making solar cells has been governed by two factors: (i) the theoretical considerations of optimum E_g , as described in Section IV-A-1 above, and (ii) the state of materials technology for the candidate compounds. Generally, of course, the theoretical considerations have been dominant, and the research effort has frequently been aimed at making good the deficiencies of the materials technology. It is a remarkable fact that in no case has this effort been sufficiently successful to provide a serious competitor for the silicon solar cells in use today, for conversion efficiency and cost.

1. Gallium Arsenide

With both of the above considerations in mind, an early subject for investigation and one which has provided the most promising cells, has been GaAs. As mentioned in III-C-3, the first report of a cell made of this material was by Gremmelmaier, who obtained a cell on a polycrystalline wafer showing a sunlight conversion efficiency of 4%.

The next group to enter the field was that working under Rappaport at RCA Laboratories, and work in these laboratories and at others in RCA, has provided almost the entire Western effort in this field. The work was initially funded by the Signals Corps (152) during the period April 1955 to August 1957. Several materials were investigated (CdTe, InP, experimentally and others theoretically), aside from GaAs. Difficulty was experienced in obtaining GaAs wafers of sufficiently low impurity concentration and with adequately large single crystals, so the results were variable. However, 1-mm² cells formed by Zn, Cd, and Hg diffusion into wafers cut from ingots showed efficiencies up to 6.5%, and later cells of about 20-mm² formed

by Cd diffusion showed efficiencies of up to 3.4%. Initial difficulties with contacting were eliminated, leading to cells with reasonably low R_S losses. However, measurements showed I_0 to be 10^5 times larger than that predicted by diffusion theory, and to vary with temperature as $\exp(E_g/2kT)$ rather than $\exp(E_g/kT)$. This reduced the working voltages below those theoretically predicted, though not disastrously so, V_{oc} values up to 0.9 V being seen. However, the I_{sc} values were nearly a factor of ten lower than those predicted. This was found to be due not to surface recombination, but to low minority-carrier lifetimes. At the time these were ascribed to non-stoichiometry and crystal defects in the GaAs, whereas they are now known to arise from direct recombinations between free holes and electrons. In addition to these diffused-junction cells, small-area junctions were also made by alloying of Zn or In dots, followed by chemical removal of the bulk of the alloying material to expose the p-n junction. Naturally, such a technique would not, in general be applicable to large-area cell manufacture. Jenny, Loferski, and Rappaport reported briefly on the results obtained, in 1956 (153), also giving a spectral response curve for the Cd-diffused cells. This curve showed the onset of photo-current at a wavelength corresponding to $E_g=1.35$ eV, as would be expected.

Soviet workers were quick to take an interest in the possibilities of GaAs photo-cells, as witnessed by a report by Nasledov and Tsarenkov (312) in 1957. GaAs cells were prepared in n-type polycrystalline wafers by diffusion of Cd, reference being made to the RCA work. Diffusion was performed in a sealed ampoule in which two temperature zones existed, the GaAs wafer being at 1050°C , and the second zone being at 850°C to maintain the vapor pressure of Cd at a value sufficiently low to prevent attack of the GaAs surface. Results comparable to those of the RCA group were obtained, the spectral response being shown, and an efficiency of 2.8% for a device 1.8 mm^2 being obtained. However, I_{sc} values of up to $8.3\text{ mA}\cdot\text{cm}^{-2}$ were obtained (rather higher than the RCA work), whereas the poor contacts used (a pressed tin contact to the diffused layer) resulted in a larger R_S , with a corresponding power loss. The polycrystalline wafer used for this study indicated that here also difficulty was being encountered in obtaining starting material of adequate quality.

In 1957, Gremmelmaier (313) reported further work involving GaAs cells, in which γ -irradiation was used to excite a p-n junction, and from these measurements a diffusion length was calculated. This was found to be $8\mu\text{m}$ for a diffused junction in GaAs, with a maximum lifetime of 9 nanosec.

Meanwhile, the work at RCA continued, under further funding by the US Army Signals Corps(192). The objective of this work was to make cells capable of operating at higher temperatures than silicon cells. The main research done was on cell fabrication techniques, to evolve manufacturing methods capable of yielding cells with an area comparable to silicon cells, and with sunlight conversion efficiencies of 8%. Work on GaP-GaAs, CdTe, and CdSe cells was also done under this contract, and will be described later.

The work on GaAs covered three main areas during the period July 1958 to October 1960:

- (i) Diffusion process parameters such as diffusion time, temperature, and dopant material and its concentration were varied in a systematic way to maximize cell efficiency. It was found necessary to maintain a low surface concentration of dopant during diffusion to prevent attack and alloying of the GaAs surface. When the sealed ampoule technique was being used for diffusion, a limited amount of dopant was weighed into the ampoule to provide the desired vapor pressure at the diffusion temperature (cf. the two-zone diffusion ampoule technique used by Nasledov). Zn and Cd were used for this work, and the best results were obtained with low diffusion temperatures ($\sim 700^\circ\text{C}$), and junction depths of $\sim 1\ \mu\text{m}$. It also proved necessary to control carefully the cooling rate at termination of the diffusion, too rapid cooling leading to blistering of the GaAs surface by rapid out-diffusion, too slow cooling leading to alloying of the GaAs surface. Later in the work, the open-tube diffusion technique was used, in which the dopant (Zn) was passed over the wafers in a stream of carrier gas, thus allowing greater control of the diffusion ambient during processing. Problems were encountered in obtaining a sufficiently high surface concentration in this case, but again control of the rate of temperature drop at the end of diffusion was found to be necessary, and this could be controlled to provide the required surface concentration while still avoiding alloying. The best results from ampoule and open-tube processes were comparable, the cells having sunlight efficiencies of 7% with areas of $0.7\ \text{cm}^2$ and junction depths of $1\ \mu\text{m}$ or less.
- (ii) Measurements of spectral response were combined with theoretical analysis as described in Section IV-A-1 to provide estimates of minority-carrier lifetime and diffusion lengths. Although this work was hampered by lack of accurate optical absorption data for GaAs, it was estimated that a minority-carrier lifetime of 10^{-10} sec was being obtained in the finished cells, and this was causing a serious reduction in collection efficiency. To deal with this problem, post-diffusion treatments to improve minority-carrier lifetime were investigated. These involved low-temperature diffusion of Cu or Ni into the cell at about 300°C , but the results were largely negative. The most effective way of improving the collection efficiency was found to be reduction of the junction depth by a combination of shallow diffusion and post-diffusion surface etching.
- (iii) Measurements were made of cell efficiencies at high temperatures and after 8.3-MeV proton irradiation, and the results were compared with those obtained on silicon cells. With the discovery of the natural radiation belts surrounding the Earth, radiation resistance had become an important parameter in solar cell studies. Radiation was found to lower

cell efficiency by introducing defects which lowered minority-carrier lifetime and mobility, thus reducing minority-carrier diffusion length. Since silicon cells required a large diffusion length to overcome the low optical absorption coefficient of the material, it was clear that such cells were easily damaged by radiation. It was hoped that GaAs, with its intrinsically high optical absorption coefficient, and thus a less stringent requirement for large minority-carrier diffusion lengths, would prove more radiation-resistant. The rate of loss of efficiency with increasing temperature for the GaAs cells was not found to behave as theoretically predicted, but a performance superior to that of silicon cells was seen. Thus, a GaAs cell of 7% efficiency at room temperature provided better efficiency above 150° C than a silicon cell with 10% efficiency at room temperature. The radiation-resistance measurements indicated that the GaAs cells were more resistant to radiation damage than silicon cells, but since the starting efficiencies of the GaAs cells were low (~ 3%), the results were not considered to be of great significance. The early results of this work were also reported at the 13th Annual Power Sources Conference in 1959 (314). The behavior of I_0 with increasing temperature was described as being the cause for the cell efficiency variation with temperature not following the theory, as was initially reported during the earlier work (152).

Further progress was reported a year later at the 14th Annual Power Sources Conference (315), the results already described being presented, but in addition some performance data were given for the cells now being made by Lamorte's group working at RCA's Somerville plant, under the sponsorship of the USAF (316). This contract commenced in April 1959 and was concluded in May 1962. Building on the exploratory work done at RCA Laboratories, production techniques were developed for cell manufacture, and the area capability and conversion efficiency were greatly improved. This work was reported in detail and has been the only major industrial program applied to GaAs cell development.

A major effort was applied to growing suitable starting material in the form of single-crystal GaAs ingots from which 1cm x 2 wafers could be cut with a minimum of waste. This involved refinement of the Bridgman technique, using a seed to avoid polycrystallinity and supercooling. A progressive freeze was obtained by moving the furnace relative to the ampoule to provide orderly and slow growth, a point found necessary to improve the crystal quality by minimizing defects. Treatment of the quartz ampoule inner surface to minimize wetting and resulting mechanical stress in the crystals was also found to be necessary.

Most of the crystals used were germanium-doped, a few being tin-doped, both providing n-type base material. The ingots were grown with the (111) axis along the ingot, so that slicing across the ingot was used to provide wafers with (111) planes exposed. The slices were polished before diffusion, and chemical polishes were

found to yield consistently better cells than mechanical polishes, probably by giving less work damage. Initially, the sealed-ampoule diffusion system was used but an open-tube process was quickly adopted because of the improved control possible with this system. Various furnace geometries were used in an effort to optimize the diffusion process. The majority of the best cells were made in two types of furnaces, one a resistance-heated tube furnace, the other using a radiant-heating system. Results showed the latter to give the best results by a small margin. The resistance-heated tube furnace thermal mass set a limit on the heating and cooling rates which could be achieved, whereas the radiant-heating system, in which the wafer was heated directly by radiation from a hot body, was found to provide much more rapid heating and cooling cycles. This made possible the diffusion of much shallower junctions, using a short high-temperature cycle with high surface concentration of diffusant. (This may be contrasted with the original work done at RCA Laboratories, in which shallow junctions could only be formed by low-temperature diffusion). The radiant-heating technique was also felt to minimize cell contamination, by having the GaAs at a higher temperature than the furnace walls. However, slice temperature control in this type of furnace was found to be more difficult than in tube-type furnaces, leading to a greater spread in cell characteristics.

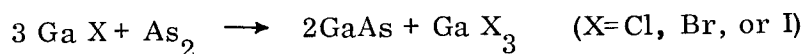
The etching process originally used by RCA Laboratories to reduce the surface region thickness was also further developed. The principal difficulty encountered here was the provision of controls to stop the etching once the optimum surface region thickness had been reached. (The optimum represents the best trade-off between surface region sheet resistance and collection efficiency, as described in Section IV-A-1). Initially this was done by etching briefly, checking the cell characteristic, etching again, checking, etc., until the efficiency maximum was reached. Clearly, such a technique could be applied to production only with difficulty, but a fixed-time etch process was found not to give adequate reproducibility. Eventually, a system was devised whereby the cell current (I_{sc}) was monitored continuously during etching, the process being terminated on reaching the I_{sc} maximum. Interestingly, it was found that this etching caused changes in the diode characteristic, since the junction was within a diffusion length of the surface, so that surface recombination influenced the conduction.

Contacts and grids were applied to the cells by vacuum deposition of silver followed by solder coating using preformed solder strips to avoid the dipping process, which had been found to severely degrade cell performance. Finally, an antireflection layer of a $1/4-\lambda$ SiO coat was applied by vacuum evaporation.

Over the three-year duration of this work, the cell efficiency steadily improved, moving from the feasibility-study cell types developed by RCA Laboratories (0.7 cm^2 , 7% efficiency), to a 2-cm^2 cell with a yield curve peak at 5.5% (1959-60), 7.5% (1960-61), and 8.5% (1961-62). The maximum cell efficiency seen was in the 13 to 14% interval. Detailed measurements of the variation in conversion efficiency

with temperature confirmed the initial RCA Laboratories' results, the cell performance falling by 0.02 to 0.03% per C° for GaAs, compared with 0.035 to 0.045% per C° for silicon cells. The behavior of cell performance under proton irradiation was also measured. The critical flux (required to cause a degradation of 25% in cell efficiency) was found to be in the interval 1.5 to 6×10^{12} 17-MeV protons cm⁻² for the GaAs cells, compared with 1.5 to 2.0×10^{11} cm⁻² for n/p silicon cells with similar initial efficiencies. Another point of comparison between GaAs and silicon cells was brought out by the radiation work. This showed that the matched load for the GaAs cells changed by only 5% under an irradiation dose of 10^{12} 17-MeV protons cm⁻², whereas for n/p silicon cells under the same dose the matched load resistance had changed by more than 50%. Thus, operating under fixed load impedance conditions (as would be normal on a spacecraft), the GaAs cells would provide a considerably more stable power supply under irradiation.

Research on various alternative cell formation processes was also pursued under this work. A small number of n-on-p cells were made, and although these had a lower efficiency than the p-on-n cells (2.3%), it was felt that this type of cell would be worthy of further study, since the electron mobility of GaAs is much higher than the hole mobility, and thus the surface layer resistance in an n/p cell should be correspondingly lower than in a p/n cell with the same junction depth. (It would appear that the minority-carrier diffusion length should be greater in the p-type base also, for the same reason. This should act to increase the collection efficiency, a point not mentioned in the reports. However, the potential efficiency increase available here would be small because of the already high collection efficiency, and might well be outweighed by the increase in cell resistance from the increased base region resistivity.) Another cell process which received rather more attention was the epitaxial growth of GaAs on GaAs, to form the surface layer. Two deposition systems were used, both based on the halide transport process:



In the first, the reactants were formed by passing HCl over heated GaAs. In the second, GaCl was formed by passing GaCl₃ over heated Ga, with the arsenic being sublimed from the solid. Although the cells made by this technique exhibited low efficiencies, this was felt to be a reflection of the processing technology rather than a fundamental limitation. The control of the carrier concentration which is possible in the GaAs grown this way is particularly interesting, a point which has been exploited more recently by groups working on other types of GaAs devices. Gobat, Lamorte, and McIver (317) and Lamorte (318) published summaries of the results obtained, during 1962. However, the maximum cell efficiencies seen were higher than those quoted in the Final Report (316).

An efficiency of 13%, and a V_{OC} value of 0.96 V (not necessarily in the same cell) under 100 mW.cm⁻² sunlight, were quoted (317).

Meanwhile, the Soviet work under Nasledov continued (319), and at the end of 1959 had apparently reached a status comparable with that of the RCA work, though it is not possible to make an exact comparison, since the Russians do not give cell areas or conversion efficiencies. However, the cells were being made on polycrystalline GaAs (indicating that single-crystal GaAs was less readily available in the USSR than in the U.S. at this time.)

Further, the junction depths quoted ($\sim 10 \mu\text{m}$) militate against a good cell efficiency, which is borne out by the poor blue response of the cells in the spectral response curves shown. The cells were apparently made by the same techniques as those reported earlier (diffusion of Zn or Cd into n-type base material of 10^{17} carriers cm^{-3}). However, the cell contacting techniques had improved, evaporated Ag contacts to the p-layer being used (cf. the work of RCA Somerville, above).

In 1960, the results were published of research at TI laboratories (Dallas), apparently internally funded (320). The cells were of structure similar to those made at RCA Somerville, having a 1×2 cm n-type base with a shallow Zn-diffused junction, and an antireflection $1/4\text{-}\lambda$ coating of vacuum-deposited SiO_2 . However, contacts were made by the electroless nickel process, and this probably was a major contribution to the rather large R_s value which can be deduced from the I-V characteristic shown. The current density for the cells was about $13 \text{ mA}\cdot\text{cm}^{-2}$, comparable to that of the RCA work in 1962. An efficiency of 7% was quoted for the TI cells, which is almost exactly the same as that for the RCA cells of this period (1960).

The original research at RCA Laboratories continued during the period November 1960 to October 1961, again under Signals Corps funding (321). Only a portion of this contract effort was devoted to GaAs cells, radiation studies on silicon cells also being performed. A solution-regrowth process was investigated for making p-n junctions in GaAs cells. This involved immersion of the base wafer in a solution of GaAs and dopant in gallium at a high temperature ($\sim 700^\circ\text{C}$); the temperature of the solution was then raised slightly to dissolve a little GaAs from the wafer surface to perform a cleaning operation, followed by a slight lowering in solution temperature to cause precipitation of GaAs onto the wafer surface, the regrown material containing dopant to provide a conductivity type opposite to that of the base wafer. In this way both p/n (Cd or Zn in solution) and n/p (Sn in solution) cells were made. This provided a surface layer with a very high carrier concentration (5×10^{18} to $2 \times 10^{19} \text{ cm}^{-3}$), but the resulting poor operating characteristics of the diodes gave low efficiencies. Also, difficulty was encountered in obtaining uniform regrowth, so that large-area cells were not obtained.

GaAs cells from the RCA Somerville production line were used in radiation damage studies. Under bombardment with 800-keV electrons, the degradation was found to be the same as that for n/p silicon cells, the critical flux (to produce a drop of 25% in efficiency) being about $2 \times 10^{16} \text{ cm}^{-2}$. The main efficiency loss occurred by a

drop in I_{SC} . Under bombardment with 19 MeV protons, however, the cells were considerably more resistant than n/p silicon cells, with results similar to those obtained by the RCA Somerville group (see above).

In 1962, the Astro-Electronics Division of RCA, under contract to the USAF, provided information concerning array manufacture using GaAs cells (322). The results were pertinent to systems fabrication only and were therefore beyond the scope of the present work. The status of GaAs cells was compared with that of silicon and other cells by Loferski in 1963 (323), and the reasons for the efficiencies seen were discussed. In particular, the significance of the low minority-carrier lifetimes was now understood, the work of Hall (324) and Mayburg (325) being quoted, concerning the likelihood of direct recombination processes occurring in GaAs. The fact that GaAs is a direct bandgap material was now appreciated, so that lifetimes greater than about 10^{-8} sec could not be expected in material with a carrier concentration of 10^{17} cm^{-3} . However, Loferski calculated that the short diffusion length value resulting from this would be offset by the optical absorption coefficient, so that in principle (i. e., with no surface recombination), collection efficiencies close to unity should still be achievable. In practice, the best GaAs cells had an I_{SC} density of $17 \text{ mA} \cdot \text{cm}^{-2}$ (the calculated theoretical maximum being $32 \text{ mA} \cdot \text{cm}^{-2}$) under $100 \text{ mW} \cdot \text{cm}^{-2}$ sunlight illumination. Loferski quotes the maximum conversion efficiency seen as being 13%, corresponding to the data given by Lamorte (317).

By now, the greatest amount of money being spent on solar cell research was concerned with radiation testing, and comparisons between silicon and GaAs cells under various radiation conditions could be made more accurately. Wysocki (326) published results on GaAs cells irradiated under both protons and electrons with various energies, obtained with the support of the USAF (322) and NASA (259). These showed that under high-energy electron (5.6 MeV) and proton (1.8 to 9.5 MeV) bombardment, the critical flux for GaAs cells was a factor of ten higher than n/p silicon cells. For 0.8-MeV electrons, the performance of the two cell types were comparable, as mentioned above. For low-energy protons (0.1, 0.4 MeV), however, the GaAs cells were more susceptible to damage than n/p silicon cells. Wysocki attributed this behavior pattern to the fact that the GaAs cells operated by collection from the region of the cells very close to the illuminated surface, so that particles absorbed primarily in this region (i. e., low-energy particles) would have a large influence on cell operation, whereas more penetrating radiation would have little effect. In silicon, on the other hand, the major response came from the base region of the cell, so that the converse would be true. The results fitted with this picture, which was also supported by spectral response measurements. These showed that the silicon cells lost mainly red response under irradiation since the longer wavelengths were absorbed less strongly and thus generated carriers deep in the base region. For the GaAs cells, however, the blue response was mainly lost under irradiation, since the longer wavelength photons could penetrate sufficiently far into the cell to be absorbed near the junction. Thus, a coherent picture of radiation damage in GaAs cells was established.

Progress in the Soviet work was reported by Gutkin et al. in 1962 (328). The original junction formation methods (Zn or Cd diffusion in quartz ampoules with two regions at different temperatures) were still in use, but the starting material was now Czochralski-pulled single crystal with 10^{17} electrons·cm⁻³. (This should be contrasted with the Bridgman technique being used at RCA Somerville; unfortunately, no process details are given by the Russians but the solution to the problem of maintaining an adequate As₂ pressure in the growth chamber in equipment which requires rotating and sliding motions of the pulling head is a difficult one.) The cells were 5.5-mm-diameter discs, with indium contacts: the discontinuance of the use of silver electrodes (reported earlier) was not explained. Although performance measurements were not reported, it appears that the cells were of low efficiency since the junction depths were still ~ 10 μ m, and the spectral response curves show a correspondingly poor blue response. Measurements of spectral response were made over the temperature range 78 to 417°K, the operating temperature presumably being limited to below 429°K (156° C) by melting of the In contacts. The junction I-V characteristics were measured and found not to obey the Shockley or Sah, Noyce, Shockley theories, it being postulated that the effects seen were due to surface recombination effects, as had been suggested by Lamorte's work. In addition to the photovoltaic work, photodiode characteristics were also described, suggesting that the devices were intended for detectors as much as energy converters. Only in 1963 (329) was any mention made of Russian devices in which the shallow junction (~ 1 μ m) characteristic of efficient cells was used. This later work was entirely devoted to the use of the devices as photodiodes, however.

In 1962, further support for the RCA Somerville GaAs cell production facility was obtained from the USAF (330), and work aimed at optimizing production processes using a pilot line was pursued during the period June 1962 to February 1964. During this period, the GaAs crystal-growing process was modified, to replace the Bridgman technique (in which progressive freezing was obtained by relative motion between the ampoule and the furnace), with a gradient-freeze technique in which furnace and ampoule were fixed. Multizone temperature control in the furnace was used with programmed power supplies to move a temperature profile along the ampoule, thus inducing progressive freezing of material from the seed onwards. This produced more reproducible material, and enabled production volume to be increased. Small changes were also made in the arsenic overpressure (governed by the cold zone temperature in the ampoule), to reduce boat wetting, and in the selection methods for seed crystals, to improve GaAs quality.

The radiant-heating diffusion process investigated earlier did not prove to be capable of being adequately controlled, so the original open-tube technique was used. This involved a 13-minute diffusion at 720° C in a nitrogen atmosphere, using Zn as diffusant. The junction depth thus produced was 1.5 μ m on the average. After etching to expose the base material at the back of the slice, the cells were cut to size with an ultrasonic tool. Both grids and back contacts were deposited by vacuum evaporation of nickel and silver, followed by a sintering operation at 600° C under a

hydrogen atmosphere. Most of the cells were equipped with nickel tabs to facilitate array construction, the tabs being attached with a Ag-Pb eutectic solder. The surface thickness was then reduced to $\sim 0.5 \mu\text{m}$ by etching in $\text{KOH}:\text{H}_2\text{O}_2$ solution using the etch-and-test process developed earlier (see above). Finally, an antireflection coating of SiO_2 was vacuum-evaporated onto the cells. A large effort was made under this work to develop trays, jigs, etc., to maximize the efficiency of the manufacturing processes. Many details of these together with statistical information on the pilot line operation were given in the Final Report. Fundamentally, the cells were the same as those manufactured under the previous contract. However, the yield curve on the pilot line peaked at 9.5% conversion efficiency at the end of the program (cf. 8.5%, 1961-62), with a noticeably smaller spread in cell characteristics than earlier. Testing of the cells under various operating conditions generally yielded no surprises, the cells being stable. However, for operating temperatures above 200°C , degradation in V_{OC} was noted during the first few hundred hours of operation, typically from a starting value of 0.86 V down to 0.60 V, and with a small decrease in I_{SC} . This was found to occur only in cells with tabs, and to be caused by degradation of the p-n junction under the contact area. It was felt that this indicated that the tab attachment method needed modification, but it was concluded that the cell was intrinsically stable. Operation of the cells at high temperatures and at high light levels (up to 700 to 800 $\text{mW}\cdot\text{cm}^{-2}$) showed the cells to be much superior to n/p silicon cells under these conditions, as was expected. In addition, radiation-resistance measurements on the cells were quoted, the results being those reported by Wysocki (326). Finally, it should be noted that although the pilot cells were all 1 cm x 2 cm units, a small number of experimental 2 cm x 2 cm cells were also made, which showed efficiencies up to 10.2%.

In spite of the great advances made in GaAs cell technology and performance during this program, the cells could not compete with conventional silicon cells for normal space mission requirements, so that further development has largely ceased in the period 1964 to the present. But a few notes on the research are in order. The Russian work under Gutkin continued with comparisons between theoretical and experimental spectral response curves for cells with surface layer thicknesses down to $1 \mu\text{m}$ (331). Work aimed at investigating the influence of crystal orientation on the quality of p-n junctions (332) showed that the orientation did not affect the diffusion within the limits of experimental error. However, the report was notable in that Bridgman crystals were now being used in place of the Czochralski material used earlier, as mentioned above. Further work by Gutkin (333) showed that the spectral response of GaAs p-n junctions at photon energies considerably higher than the band edge (measurements were made up to 5.4 eV) indicated a fundamental change in the quantum efficiency of the absorption process. The band structure was examined to consider the various transitions which could occur in the absorption. It was concluded that the most likely process was impact ionization, in which an electron excited into the conduction band had enough energy to cause a valence-to-conduction band transition in a second electron, thus creating another hole-electron pair. Further measurements on low-energy proton irradiation of GaAs cells were reported by Wysocki et al. (334). As before, the GaAs

cell behavior showed a rapid loss of I_{sc} under irradiation, and the measurements allowed a model to be developed for predicting the effects of irradiation on performance for the range of proton energies below 6 MeV.

This is then the present situation for GaAs single-crystal cells. The most efficient cells made had a structure closely analogous to that of conventional silicon cells, in that they consisted of a shallow p-n junction formed by diffusion into homogeneous base material, with gridded surface contacts, and SiO antireflection coatings. Although the cells have proven advantages over silicon for use in high-temperature and/or radiation environments, the cell costs remained more than an order of magnitude higher than for silicon cells, partly because of the high cost of starting material and partly because GaAs is inherently a more difficult material to work with than silicon. Hence, there is no production of GaAs cells at the present time, and research on such cells has all but ceased, except for radiation damage investigations.

2. GaP and GaP-GaAs Cells

It was realized early in the research on GaAs cells that a potential difficulty would be a loss in collection efficiency by surface recombination, because the high optical absorption constant caused most carrier pair production within $1\text{ }\mu\text{m}$ or so of the surface. Since it had been established that GaAs-GaP alloys had good semiconducting properties, there appeared to exist the possibility of making a cell consisting of a p-n junction in GaAs, with the front surface of the cell consisting of layer of GaP grading through GaP-GaAs alloy to the base GaAs. The band diagram of such a cell would be as shown in Figure 63. Thus, the GaP layer would act virtually as a passive part of the cell, providing an optical "window" allowing all photons with energies less than 2.2 eV to be absorbed in the junction region of the cell, where the field gradients existing because of the graded bandgap in the alloy should aid the collection process. Photons of energy $>2.2\text{ eV}$ would be absorbed in the surface layer, and although some of these might diffuse to the junction, it was assumed that most would be lost by surface recombination. However, because of the solar spectral distribution, this would not cause any great loss of power in the device.

Experimental attempts to make a device operating along these lines were first made by the RCA Laboratories group, under the auspices of the GaAs cell work (152, 321). In addition, a group at the Eagle-Picher Laboratories obtained ARPA support to specifically investigate this type of cell (335-337). Both groups approached cell fabrication in the same way, making the GaP layer by diffusing P into GaAs, the As out-diffusing from the surface region of the GaAs and being replaced by P. X-ray diffraction studies by the RCA group established that a surface layer of GaP could indeed be formed this way, and both groups obtained working cells. However, the efficiencies were low ($\sim 4\%$), and although these were comparable or better than the regular GaAs cell efficiencies at the beginning of the work, the GaAs cells soon improved beyond what could be achieved with the GaP-GaAs cells, so that the alloy

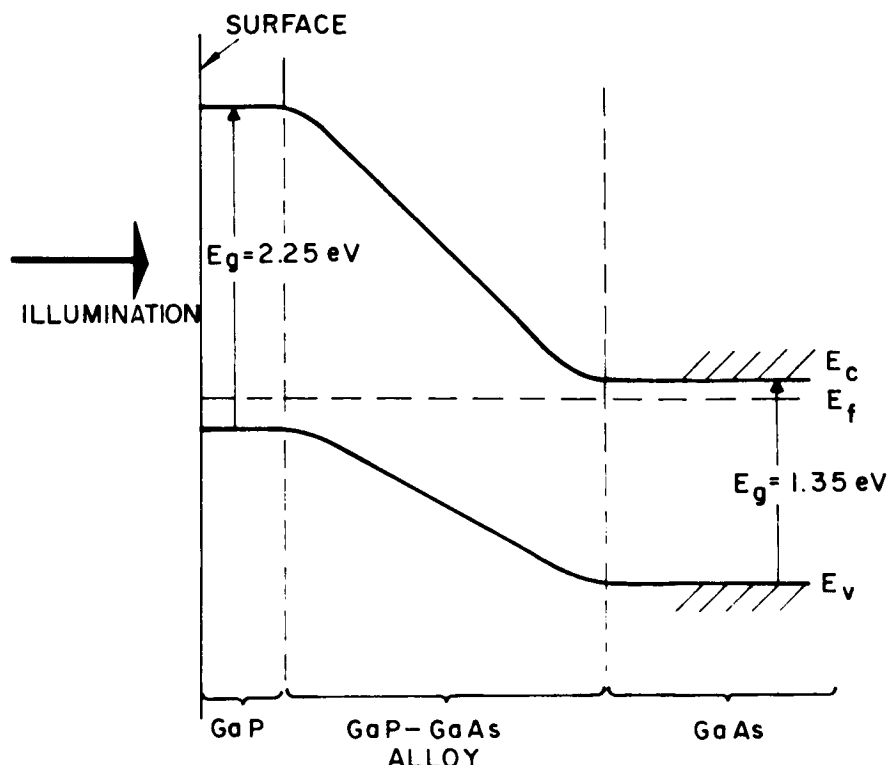


Figure 63. Band structure of a GaP-GaAs heterojunction solar cell

approach lost its initial momentum. However, the RCA Laboratories group continued to investigate the possibilities for several years, and similar work was done at RCA Somerville (316).

In addition, the RCA Laboratories group experimented with GaP cells made on pure GaP base material (191, 315). Although the theoretical maximum efficiency of this material is only 10%, as was shown by the analysis done under this work (185), the anomalous response of the CdS cell had demonstrated that such an analysis might not be applicable to all semiconductors. However, the GaP cells which were made showed only the theoretically expected response (to photon energies exceeding $E_g = 2.25$ eV), so that the device would only have application at very high temperatures ($\sim 500^\circ\text{C}$) where other semiconductors could not be used. The GaP cells made at RCA Laboratories exhibited V_{OC} values up to 1.2 V, but showed low I_{SC} values, due partly to poor GaP and partly to contact resistance problems, it being difficult to make good ohmic contacts to large-bandgap semiconductors. Extensive work on GaP, including observations of the photovoltaic effect, were made by Grimmeis of Philips Laboratories, Aachen, in 1960 (338). Although this work was done with point-contact junctions rather than large-area p-n junctions, the spectral response results are relevant to solar cells. These measurements showed that although the major peak in the photovoltaic response occurred at 4200 Å, as would be expected from the E_g value, a second response occurred in the wavelength region 5000 to 7000 Å, with a peak at ~ 5600 Å. This extrinsic response was believed to occur by the absorption of photons by two-step processes, via intermediate levels existing inside the forbidden bandgap, as shown in Figure 64. The

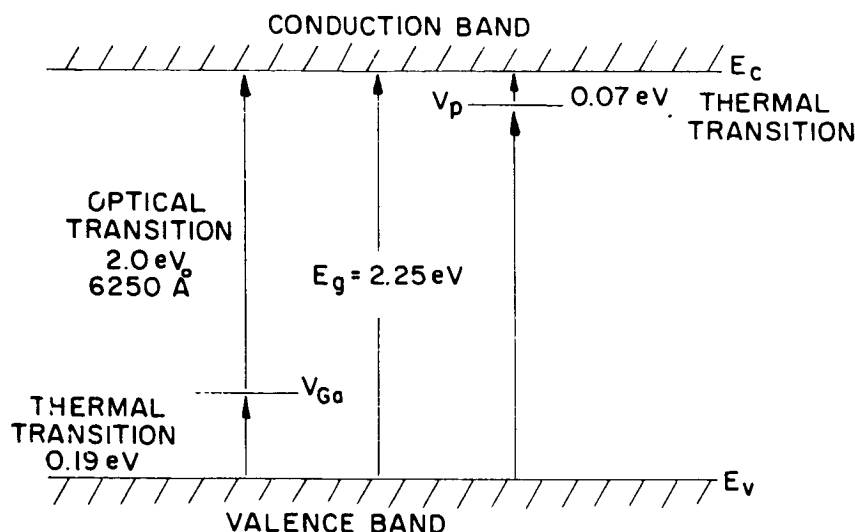


Figure 64. Transitions occurring in a GaP cell to cause extrinsic spectral response, after Grimmeis

intermediate levels were thought to arise from Ga and P vacancies. Because a photovoltage was seen even when the point-contact was shielded from the light, it was concluded that the photovoltages were being developed at p-n junctions between randomly occurring p- and -n-type regions in the crystals. Such an extrinsic response implied that the analysis of Loferski for efficiency vs. E_g may indeed not apply to GaP, as had been postulated by the RCA group.

The largest program to develop GaP solar cells was a contract between Monsanto Research Corporation and NASA, during June 1963 to August 1964 (339, 340). Because of the difficulty in obtaining GaP in single-crystal wafer form with adequate purity, this work was done with layers of GaP grown on GaAs substrates. The deposition process used was the same in principle as that used by the RCA Somerville group for the epitaxial growth of GaAs, described above, using the halide transport reaction. However, the Monsanto group aimed at producing thick GaP layers which could be self-supporting; the maximum GaP layer thickness achieved was $460\text{ }\mu\text{m}$, though most cells were made with GaP thickness of less than $100\text{ }\mu\text{m}$, and in some cases as low as $10\text{ }\mu\text{m}$ or less. Doping of the epitaxial material with Te, Zn, and Sn was investigated, but the major effort was spent on lowering the impurity concentration, and nominally undoped material was n-type in the range 10^{16} cm^{-3} or lower. Cells were made in this nominally undoped material by diffusion of Zn or Cd in a sealed quartz ampoule at temperatures generally around 800 to 850°C , to produce shallow junctions (typically $1\text{ }\mu\text{m}$). Difficulty was encountered in controlling the results of the diffusion process, and this was ascribed to compensation in the starting material.

Contacts to the GaAs base were made with vacuum-evaporated Au-Sn alloy, and to the surface of the GaP by vacuum-evaporated Ag. Most cells were then etched in aqua regia (with the contacts masked) to improve I_{sc} , presumably by reducing surface recombination and layer thickness. Antireflection coatings were not used.

The cells generally had areas of 0.1 to 0.5 cm², and measurements were made of electrical properties over a temperature range of 25 to 500°C, and of spectral response. Two distinct families of cells were made by apparently identical processing. One cell type exhibited only the intrinsic spectral response, with a peak at 4700 Å, corresponding to the expected E_g , while the second showed principally an extrinsic response, with a broad peak at 7000 Å. The intrinsic cells had V_{OC} values 1.0 to 1.35 V and I_{SC} values of 2 mA · cm⁻², whereas the extrinsic cells had V_{OC} values around 0.7 V, and I_{SC} values up to 5.0 mA · cm⁻² in 94 mW · cm⁻² sunlight. The best cell was of the extrinsic type, with an efficiency of 2.5%, and the best intrinsic cells had efficiencies of 1.1%. The intrinsic cells were found to have V_{OC} values less than theoretically predicted, but the rate of fall in V_{OC} in both cell types was found to be close to the theoretical value of $3 \times 10^{-3} \text{ V} \cdot ^\circ\text{C}^{-1}$. Thus it was verified that the intrinsic cells were capable of operation up to 350°C, at which temperature the best V_{OC} value seen was 0.4 V.

This work therefore confirmed that GaP cells could indeed exhibit extrinsic response, but could also be made to behave in a wholly intrinsic fashion. This should be contrasted with the behavior of CdS cells, which have $E_g=2.4 \text{ eV}$, but which always exhibit extrinsic behavior with an effective $E_g=1.2 \text{ eV}$. The Monsanto work did not make clear the nature of the mechanism of the extrinsic response, though there is no reason to doubt that this would be a two-step excitation, either involving one thermal and one optical transition (after Grimmeis) or two optical transitions. The nature of the impurity causing the intermediate level was not known, but it was provisionally identified as due to oxygen. It is notable that a photovoltaic response from the GaAs-GaP interface was sought and not found; its absence is surprising. However, experimental results with cells from which part of the base GaAs had been removed appear to rule out the possibility that the extrinsic response arose at this heterojunction.

In the follow-on contract (341, 342) further work was done along the same lines, a major effort being made to form high-purity GaP. The cell efficiencies were improved slightly, the best intrinsic cell having an efficiency of 1.3% under sunlight at room temperature, and a $V_{OC} = 0.44 \text{ V}$ at 350°C, with an area of 0.14 cm². The good high-temperature behavior of these cells suggested their use under concentrated sunlight, and the efficiency was found to increase markedly under high-intensity illumination, a value of over 5% being found at 400 mW · cm⁻², compared with 1.3% for the same cell at 80 mW · cm⁻². The efficiency improvement was due to a rapid rise in I_{SC} above 300 mW · cm⁻². This cell was made on alloy material with composition GaAs_{0.43}P_{0.57}. The cause for the superlinear dependence of I_{SC} on illumination intensity was not known. For normal use, however, the cell efficiencies remained low, so that the work was discontinued, and there has been no work on GaP solar cells done in the West for the past two years.

However, recent reports have been made indicating that Gutkin's group at the Joffe Physicotechnical Institute at Leningrad, who worked for some years on GaAs cells (see above), have now taken an interest in GaP-GaAs cells. In 1965, Kagan et al. (343) reported experiments similar to those done by the RCA and Eagle-Picher groups some years earlier. However, the junction diffusion followed the GaP layer formation in the Russian work, the converse sequence being used in the US work. The GaP layer was formed by replacing As with P by diffusion into GaAs base material, a layer 5 to 7 μm thick being formed which was graded from pure GaP at the surface to pure GaAs in the base. The junction-formation diffusion was done with Zn in a sealed quartz ampoule, and a range of junction depths were produced. On measuring the spectral response of these cells, it was found that the response curve peak shifted progressively from 4700 Å (corresponding to the E_g for GaP) to 8500 Å (corresponding to the E_g for GaAs) as the junction depth increased. This correlated well with the results one would expect for this series of experiments. The temperature dependence of the cell behavior was measured from 40 to 180°C, and the I_{sc} was found to increase linearly over this range, as would be expected. The V_{oc} , however, showed a broad maximum of 0.65 V around 100 to 120°C for some cells, and this indicated that two competing processes were probably occurring, one the normal degradation in V_{oc} with increasing I_o on increase of temperature, the other a mechanism depending on the presence of traps and associated with thermal transitions in the bandgap of the GaP. Cell areas and conversion efficiencies were not quoted.

Cells similar to those made by the Monsanto group were reported by Alferov et al. in 1965 (344). In this case, the GaP was grown as an epitaxial layer on a GaAs wafer, by the halide-transport process used by the Monsanto group, but instead of the usual open-tube system, a sealed quartz ampoule was used. This contained the source wafer in a zone maintained at 700°C, with the source (polycrystalline GaP) in a zone maintained at 900°C, and CdCl_2 to provide dopant (Cd) and transport agent (Cl); the process details were given in (345). The spectral response curves, however, showed that in contrast to the Monsanto cells, the Russian devices had the p-n junction formed between the p-type GaP and the n-type GaAs, so that the spectral response was remarkably constant over the range 1.3eV (band-edge for the GaAs) to 2.2eV (band-edge for the GaP; photons with energy >2.2 would be absorbed in the surface of the GaP and would thus not reach the active junction). The devices had $V_{oc}=0.5$ V, and showed a linear dependence of I_{sc} on illumination intensity.¹³ Device areas were not quoted, and the given efficiency of 8% (for operation under "white light") is not consistent with the other data ($V_{oc}=0.5$ V, illumination of 1.5×10^{-5} W, matched load resistance 400 kilohms).

Further Soviet work on GaP-GaAs devices was reported by Gutkin et al. in 1966 (346). This work was done on devices made by diffusing P into GaAs wafers, however,

¹³Note that in Figure 2 of the original paper, curves 1 and 2 are the inverse of their appellations in the figure captions.

and thus implies a reversion to earlier techniques. Spectral response curves with two peaks (one at the GaAs band edge, one at the GaP band edge) were in general obtained, and the measurements were taken out to photon energies of 5.4 eV. In contrast to the measurements on GaAs cells (333), these measurements showed no evidence for quantum efficiencies >1 for the absorption of high-energy photons, and this was correlated with the differences between the band structures for GaP and GaAs.

This then is the present status of GaP and GaP-GaAs cells. The GaP cells show extrinsic response in some cases; this implies that the material may be worthy of further investigation, a point which will be taken up later in this work. Intrinsic GaP cells appear to have no applications at the present time, and their efficiencies cannot be expected to ever be greater than 10%. GaP-GaAs cells have generally shown low conversion efficiencies, but it appears that this is due mainly to poor materials technology, and that further development of the epitaxial growth processes which have proved so successful for GaAs, may offer further possibilities for improvement in this type of cell.

3. Other III-V Compounds

Little work has been done on the other III-V semiconductor materials compared with that done on GaAs and GaP. Of these other materials, aluminum antimonide (AlSb) has received attention principally because the theoretical efficiency calculations of Rittner, Loferski, and others indicated that the bandgap of AlSb should be close to the optimum for sunlight conversion efficiency (see IV-A-1). The earliest report of photovoltaic phenomena appears to be that of the Czechoslovak worker Abraham (347). Spectral response measurements for photoconductivity and the photovoltaic effect were obtained from polycrystalline specimens, over the wavelength range 0.5 to 1.35 μm and for temperatures from 126 to 295° K. The specimens used were freshly cleaved from polycrystalline ingots, the conductivity type and contacting methods not being indicated. It appears probable therefore that the photovoltages observed were generated either at randomly occurring p-n junctions between crystallites of opposite conductivity type or at metal-semiconductor blocking contacts. The photovoltaic response showed an almost monotonic increase (presumably in I_{SC}) as the wavelength was shortened from 1.3 to 0.5 μm . The photoconductive spectral response was quite different, showing a maximum at around 0.8 μm ; the reason for this difference was not clear. Abraham also noted that photosensitivity was lost within a few days after cleaving and could not be restored by etching.

This phenomenon is the greatest drawback to the practical application of AlSb in devices. The material is attacked by oxygen or water vapor to form Al_2O_3 or $\text{Al}(\text{OH})_3$. The oxide forms a tenacious surface layer on single crystals, and the hydrate causes polycrystalline material to decompose, although single crystals are

attacked only slowly. This phenomenon occurs even if the AlSb is stored under normal high vacuum ($\sim 10^{-6}$ Torr), so that it is extremely difficult to prepare material even for experimental use. It is not surprising, therefore, that there was little work done on AlSb for some years, while the other III-V compounds were worked on widely.

However, during the period June 1960 to June 1962, much progress was made in advancing the state of the materials technology art for AlSb, under a USAF-sponsored program at Electro-Optical Systems, Inc., Laboratories in Pasadena (348). The greater part of this work was done in developing crystal growth methods and slicing, etching, and diffusion techniques for AlSb. Only an outline of this side of the work is given here; the Final Report on this work contains a great deal of detail on the technology involved, and the reader is referred to this if such detail is required.

Commercially available aluminum was not of sufficient purity for semiconductor use, so that purification methods were evolved to provide suitable starting material. These involved a zone-refining step, which removed all impurities but oxygen and magnesium. These were removed by heat-treating the aluminum for 20 to 40 hours at 1000°C under high vacuum; the Mg evaporates, and most of the surface covering of oxide is also lost.

Special Czochralski crystal-pulling equipment was developed to allow Sb to be added to the molten aluminum at the end of the heat-treatment cycle, the seed to be immersed in the melt, and crystal growth to be completed, before the material was exposed to oxygen. At the start of the work, single-crystal AlSb was not available as seed material, and single-crystal growth was eventually obtained by selection of larger and larger crystals from polycrystalline boules from successive growths. Difficulty was also encountered in containing the molten AlSb, and only pure alumina crucibles were found to be capable of withstanding attack by the melt. Nominally undoped AlSb was always p-type, and n-type crystals were made by doping the melt with Se. It was found that if slicing could be performed fairly rapidly (a few minutes) normal wafer-cutting techniques using water could be employed, the attack on the AlSb being fairly slow. Various etches for dislocation detection, crystallographic identification, and polishing were developed.

Measurement of conduction parameters showed a maximum resistivity of $3\text{ Ohm} \cdot \text{cm}$ in the purest p-type material, which was believed to contain residual copper. The n-type material was, of course, compensated, and resistivities up to $4.5\text{ Ohm} \cdot \text{cm}$ were obtained. The highest Hall mobility for holes was $440\text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$, whereas electron mobility in n-type material was found to be only $50\text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$, reflecting the compensated nature of this material. Carrier lifetimes were found to be short, 1 nanosec or less. Optical measurements showed results supporting the belief that AlSb is an indirect energy-gap material.

A large number of diffusion experiments were performed, using Se, Te, and Sn as n-type diffusants, and Zn and Cd as p-type diffusants. All diffusion was performed in sealed quartz ampoules. Various difficulties with separate-phase formation were encountered with Se and Te as diffusants. Only certain of these materials were found to make satisfactory photovoltaic junctions, however.

Ohmic contacts also proved to be difficult to achieve, presumably because of Al_2O_3 surface films. The best results were obtained with pure In or Cd to p-type material, and In-Se alloy to n-type applied by a soldering iron. All vacuum-evaporated contacts proved to be rectifying, and plated contacts were also unsatisfactory.

Device fabrication proved to be a formidable problem. Diffused junction diode characteristics were obtained which showed A values >2 , as for most other materials, so the device characteristics were not unusual to any great degree. From the forward and reverse characteristics, the presence of a deep-lying level in the energy gap was deduced, but this is also not necessarily of great significance. However, although photovoltages above 0.6 V were obtained with point contacts, the application of large-area contacts to the back of the cells, and small ohmic contacts to the diffused surface, in every case caused a major reduction of photovoltage value. Although some I-V curves were obtained under illumination, the I_{SC} values were very small, and cell efficiencies never exceeded 0.5%.

The EOS work may be contrasted with a program of development for AlSb run at RCA Mountaintop during 1964-66, under NASA funding (349, 310). The RCA group worked with AlSb purchased from a commercial supplier (Bell and Howell), and hence the emphasis of the work was on cell fabrication rather than materials preparation. The problems of diffusion encountered in the EOS work were also met, diffusants being found to form separate-phase compounds by reaction with Sb, leaving a surface deposit which interfered with diffusion and degraded cell performance. Both n-and p-type base material were used during the earlier work, but later work concentrated on n-type. Sealed-ampoule diffusion was used, with Zn as a diffusant for the most satisfactory cells. It was found that for the short diffusion times used, the diffusion depth was much less than that calculated from published diffusion-constant data, and the actual junctions were about $2\text{ }\mu\text{m}$ below the surface. The early work (349) produced cells with V_{OC} values up to about 0.7 V, and I_{SC} values up to $3.5\text{ mA}\cdot\text{cm}^{-2}$, but low I_{SC} values for most of the cells, and the I-V curve shapes, showed that blocking rather than ohmic contacts were being obtained. Various contacting techniques were investigated, including silver-epoxy, evaporated Ti-Ag followed by sintering, and evaporated Al followed by sintering, for both n-and p-contacts. Because of this problem cell efficiencies were less than 1%. Further work on the contact problem eliminated the double-junction effect by using Pb applied by ultrasonic soldering to the n-type base. The diode characteristics were also improved by post-diffusion etching to remove surface layers. Although efficiencies of somewhat less than 3% were achieved, these cells were found to be highly unstable, degrading in V_{OC} after only a few hours either in air or in a

dessicator. Further, the junction characteristics were found to be very sensitive to edge treatments on the cells (i. e., treatments of the regions where the junction comes to the cell surface), indicating that leakage effects were a major problem; the same observations were also made in the EOS work. Spectral response measurements were made on these cells, and the results were as would be expected from the known optical absorption curve for the material. The cell efficiencies obtained were thus rather low, and the materials technology problems highly intractable, so that further work on AlSb cells has not been done. This is the present status of work on AlSb cells; bearing in mind the nature of the material, it is remarkable that even this modest success should have been achieved.

The remaining III-V compound with an energy gap in the range in which good solar conversion efficiency should be obtained is InP. The first work aimed at developing solar cells of this material was done at RCA Laboratories under a Signals Corps contract, starting in 1955 (152).

Since starting material was not available commercially, ingots were grown in-house by melting the elements in a quartz tube with two temperature zones, the lower temperature controlling the P pressure. Polycrystalline p- and n-type material was obtained, with a high carrier concentration. Diffusion was used to prepare p-n junctions, Cd, Zn and Hg being used as p-type dopants, and the best results were obtained with the latter. The best cell obtained showed $V_{OC} = 0.74 \text{ V}$ (cell area 0.2 cm^2), and a conversion efficiency of about 1%.

The cell performance was severely limited by high series resistance arising in the contacts. Some photosensitive diodes were also made by alloying Zn onto the crystal surface, but such devices were for experimental purposes only. At the time, experimental effort and results were limited by the lack of good single-crystal InP. The situation remained thus for some years, as reported by Rappaport in various papers up to 1961 (242, 189, 350, 351).

Nothing further appears to have been done on InP cells until the recent report of experimental results by Galavanov et al. at the Joffe Institute in Leningrad (352). With the general advances in compound semiconductor technology which had been made since the early RCA Laboratories' work, a big advance in cell performance was to be expected. Even so, the reported cell areas were only of 0.1 cm^2 , prepared by Zn or Cd diffusion into n-type single-crystal base material in a sealed quartz ampoule. Under solar irradiation of $70 \text{ mW} \cdot \text{cm}^{-2}$ the device showed $V_{OC} = 0.74 \text{ V}$, $I_{SC} = 10 \text{ mA} \cdot \text{cm}^{-2}$, and efficiency of 6.7%. The spectral response was also measured, and showed the expected form, with a sharp rise in response for photons with energy slightly greater than that corresponding to the band edge. However, a rapid loss of collection efficiency on going to higher photon energies (i. e., loss of blue response) indicated a deep junction, implying that the cells would be capable of considerable development to provide better efficiencies. The tone of this Russian report indicates that further work can be expected in this area, and this group appears to be alone in this field of research at the present time.

The remaining III-V compounds for which photovoltaic effects have been reported are InSb and InAs. These materials both have small energy gaps (InSb, $E_g=0.167$ eV; InAs, $E_g=0.35$ eV) so that good solar conversion efficiencies cannot be expected, and both materials are of interest primarily as infrared detectors. However, for such use the device temperature for InSb must be reduced to suppress the intrinsic conduction which is appreciable in this material at room temperature.

Results with alloyed junctions produced with Cd and In dots on n-type InSb were reported by Galavanov in 1959 (353). The diode characteristics and photovoltaic response were measured over a temperature range from 300 to 77° K, and the results showed that the photovoltage reached values of between 10 and 20 mV at 77° K and decreased rapidly at temperatures above 167° K.

Results with InAs were reported by Gutkin in 1967 (354). This work was aimed at spectral response measurements in the range of photon energies $h\nu \gg E_g$, to provide information on impact-ionization studies. The cells were made by diffusing Cd into n-type single-crystal InAs with a carrier density 0.5 to $1.0 \times 10^{17} \text{ cm}^{-3}$. The spectral response data were taken at temperatures of 100 and 295° K, and the response near the band edge was as expected, a sharp rise being seen in photocurrent for photon energies increasing beyond 0.4 eV. For photon energies > 0.8 eV, a further rise in quantum efficiency was seen, which continued to the limit of the measurement spectral range at 4.8 eV. This rise in quantum efficiency was attributed to impact ionization by electrons which have large energies imparted to them by photons with energies $h\nu > 2 \times E_g$. The results therefore correlate with the observations of this effect in GaAs, by Gutkin (333) and CdTe (355, 356) by Dubrovskii.

4. Cadmium Sulfide

The second major group of compound semiconductors from which photovoltaic cells have been successfully made is comprised of the II-VI compounds. In several cases the materials technology of members of this group is particularly well suited to the achievement of reasonable semiconducting properties in polycrystalline thin films. Hence, a good deal of the research on these materials has been done on thin-film cells, notably CdS and CdTe, and an account of this work will be found in a later section of this work. However, the initial work on CdS and CdTe, and a proportion of the subsequent work on these materials, was done on single-crystal or polycrystalline wafers of the semiconductors, and an account of this work will now be given.

The earliest of the II-VI materials to be worked on was CdS. An account of Reynold's discovery of the photovoltaic effect in CdS in 1954 has been given in Section III-C-3. Following this discovery, a program of research and development aimed at producing CdS cells for energy conversion, for use on the Vanguard satellite, was initiated at the Aerospace Research Laboratory where Reynolds' work was done, and with outside laboratories under USAF funding. Exploratory work was done at the

Harshaw Chemical Company Research Laboratories in 1954, cells with efficiencies up to 1% being made (357)¹⁴, and this work revealed the need for better starting material. Work aimed at providing this was done at Clevite Laboratories, Eagle-Picher Laboratories, and at Harshaw. By 1957, three growth methods had been developed.

- (i) The reaction of Cd vapor with H_2S at $950^\circ C$ to produce needles and small platelets.
- (ii) The growth of large crystals by sublimation from a powder starting material, in a sealed tube at about $1000^\circ C$, the crystals forming slowly on the cooler parts of the tube: this method had been developed initially by Reynolds.
- (iii) The growth of crystals from the melt, a process made difficult by the high temperature required ($1750^\circ C$), and the high pressure needed to prevent sublimation from the melt (100 atmospheres): this process was worked on by the Eagle-Picher group.

Method (ii) proved to be the most applicable to solar cells, and by 1960 the process had been refined to produce fairly reproducible results and large crystals. The process used by the Harshaw group in 1960 consisted of:

- (i) A sintering step in which the purest available starting material (usually 'luminescent grade' CdS) in powder form was heated to $\sim 600^\circ C$ under vacuum until outgassing stopped: this process removed water vapor, free Cd, and other impurities.
- (ii) A crystal growth step in which a charge of sintered material was heated in a sealed tube filled with inert gas (e.g., N_2) at a temperature of $\sim 1275^\circ C$, and CdS crystals were formed on the cooler parts of the tube ($\sim 1260^\circ$), the growth taking place over a period of some days. The details of this process were reported by the Harshaw group (358). Various dopants were used to give the required conductivity, the most successful impurities being $InCl_3$ and B. It may be noted that p-type conductivity in CdS has never been observed conclusively; most work has been done with In-doped n-type base material, mainly because this appears to give the most reproducible results in the desired range, and to introduce the minimum number of extraneous effects.

¹⁴This reference contains a brief historical account of the early work on CdS, and Shirland notes that most of this work was never published. Hence, this reference has been the only available source for some of the early work, except for Reynolds' publications referenced above.

The Harshaw work developed various methods for making the photosensitive barrier contact to the CdS. All of these involved depositing either metallic copper or a copper compound (e.g., Cu_2O or Cu_2S) either by vacuum evaporation or electroplating. The best results up to 1960 were obtained by electroplating Cu onto the cell surface using a strongly acidic plating bath, to produce a layer of finely divided copper particles which were then oxidized, followed by a final processing step at 300 to 350°C for 10 to 20 seconds. These cells were of the rear-wall type; i.e., the illumination passed through the CdS crystals to the junction, the active region being on the unilluminated side of the cell, the converse of the normal silicon-cell practice. For this reason, ohmic contact to the base CdS was made by means of a 'picture-frame' electrode, to allow the maximum transmission of light into the cell. The exact nature of the barrier was not known at the time, though it was postulated that a very thin surface layer of p-type CdS containing cuprous ions was present. The cell performance measured at this time showed efficiencies of 5%, with $V_{\text{OC}} = 0.5 \text{ V}$ and $I_{\text{SC}} = 13.5 \text{ mA} \cdot \text{cm}^{-2}$ under $122\text{-mW} \cdot \text{cm}^{-2}$ illumination. Spectral response measurements on rear-wall cells showed an onset of photovoltaic response at wavelengths between 7500 Å and 8500 Å, and a sharp cut-off at 5200 Å, caused by absorption in the base CdS. Some front-wall cells were also made, in which sufficient Cu_2O was etched away from the barrier layer to allow illumination on this side of the cell to penetrate to the junction. In these cells, the spectral response showed the anomalous extrinsic response described above, and added to this was the expected intrinsic response of the CdS absorption, which extended the response to wavelengths less than 3000 Å, with a peak around 4000 Å. The efficiency figures given in (358) are those for typical cells, it should be noted. As early as 1958, the Harshaw group had obtained efficiencies up to 7.6% under $100 \text{ mW} \cdot \text{cm}^{-2}$ sunlight in cells $1 \times 1 \text{ cm}$, with $V_{\text{OC}} = 0.5 \text{ V}$. (359).

Early interest in the extrinsic response of CdS cells was shown by several workers. Reynolds (360) proposed that the response arose from the presence of an intermediate energy level in the forbidden band of the CdS, electron-hole pairs being created by excitation of electrons from this intermediate level into the conduction band. However, to account for both the photovoltaic and photoconductive phenomena seen in CdS, Reynolds proposed that it would be necessary for this intermediate energy level to form a band rather than a set of spatially separated levels. Reynolds' experimental work had showed that the prior illumination history of the cell partially determined the photocurrents seen, and this observation correlated with photoconductivity results reported by Lashkarev et al. (361-363) in which conductivity quenching by IR, and photoconductivity enhancement with prior illumination with green light, was seen. Further work on the spectral response of the photovoltaic effect was reported by Woods and Champion of GEC Laboratories, England (364). Correlating measurements on the photoconductivity and photovoltage in copper-doped CdS these workers also concluded that impurity band conduction was occurring. They also reported the first published results on bias light measurements, in which the crystal was illuminated simultaneously by two separate monochromatic sources at different wavelengths (7000 and 9000 Å), and the photogenerated current induced by 7000 Å illumination was

found to be remarkably increased by a comparatively small amount of illumination at 9000 Å, to the degree that one photon of 9000-Å light was found to increase the photocurrent as much as four photons of 7000-Å light. (The peak of the spectral response curve lay at 7000 Å.) This enhancement effect was ascribed to an increase in the lifetime of free holes, the minority carriers in the n-type base material.

An alternative theory to account for the extrinsic photovoltaic response of the CdS cells with supporting experimental results, was first advanced by Williams and Bube (365). The experimental results were obtained with barrier contacts formed by electroplating copper and other metals, onto n-type CdS crystals. No heat treatment was used in the processing of these contacts, and, hence, it was felt that the diffusion of copper into the CdS was wholly absent, and the junction was purely a metal-semiconductor barrier. Spectral response measurements showed that the extrinsic photovoltaic response was present in these cells, though to a smaller degree (compared with the intrinsic response) than in the copper-diffused junctions being made by the CdS solar-cell groups. However, it was shown that the response in the extrinsic wavelength region increased as the copper thickness was increased (the thinnest copper layers were optically transmitting), indicating that the carriers photoexcited across the barrier were electrons photoemitted from the copper into the CdS. However, photoemission can be checked by the use of the "Fowler Plot" showing photocurrent as a function of photon energy at the threshold of photoemission (366). The form of the experimental curve obtained by Williams and Bube was of the shape expected for photoemission, but indicated a threshold wavelength of the onset of photoemission corresponding to 1.1 eV, whereas the same threshold calculated from the photoconductivity data was 0.4 eV, and the discrepancy could not immediately be explained. Further, Williams and Bube found that the extrinsic response of the cells was much reduced on heat-treating the cells in a manner similar to that used to enhance the response in solar-cell manufacture. Thus, there existed some doubt whether the positive identification of photoemission in the specimens of Williams and Bube proved that this was also the basis of operation for the CdS solar cells.

Experimental results on photovoltages seen when metal contacts to CdS were unequally illuminated were reported by Kallman in 1960 (367). Voltages up to 0.2 V were obtained, but the response was seen only for illumination with photons of energy near to or higher than the fundamental absorption edge of CdS. Hence, this effect was not of great significance for the development of CdS solar cells.

Results of Russian work on CdS photovoltaic cells were reported by Paritskii et al. in 1961 (368). These were concerned with the response time of the cells under pulsed illumination, and the authors supported the photoemission mechanism of Bube and Williams.

Bockemuehl et al. studied photovoltaic, photorectification, and field-effect modulation properties of junctions formed by diffusing Cu into photoconductive, dark-insulating CdS crystals (369). The results indicated that in these junctions two

barriers existed, one at the metal-semiconductor surface, the other in the semiconductor bulk. Under reverse bias, the space charges associated with these barriers altered to give a single dipole space-charge region, a condition which could be produced by application of a bias of less than 1 V.

It was found that under monochromatic illumination by light of a wavelength which created hole-electron pairs and thus caused a photovoltage, V_{oc} values of 0.2 to 0.4 V were seen. When a second monochromatic beam of IR was added, the V_{oc} rose to 0.5 to 0.6 V and I_{sc} also increased. However, under reverse bias sufficient to redistribute the space-charge, the IR was found to quench the photoconductivity arising from the main illumination. These effects were ascribed to the IR increasing the drift mobility of the holes by causing detrapping, which would aid the collection of the minority carriers (holes) in the photovoltaic effect, but cause a loss of space-charge in the space-charge region, leading to a reduction in photoconductive gain. [For an account of the mechanism giving photoconductive gain by minority-carrier trapping, see Bube (370).] Thus, the results of Bockemuehl et al. in providing evidence for photoexcitation from intermediate levels in the forbidden bandgap, tended to support Reynolds' proposal for the origin of the extrinsic response in CdS photocells, rather than the photoemission mechanism of Williams and Bube.

By measuring photovoltages produced when a fine light spot was moved across Cu and blocking Au contacts deposited on an n-type CdS crystal, Fabricius (371) obtained evidence that the generation of the photovoltage was localized in the depletion region of the Au-CdS contact, thus indicating that the mechanism of Williams and Bube was not responsible for the photovoltaic effect in these specimens. Since the Au-CdS and Cu-CdS contacts were produced by vacuum evaporation followed by heat-treatment to cause diffusion, whereas Williams and Bube had avoided any diffusion in preparing specimens, it was to be expected that the results of the two sets of experiments should be different.

The operation of CdS cells was also analyzed by Grimmeis and Memming in 1962 (372). Experiments were performed using diodes made by diffusing Cu, Ni, or Ag from evaporated films deposited on n-type crystals of about 1-Ohm · cm resistivity, followed by removal of the remaining metal layer by etching. Thus, it was felt that the specimens could contain only p- and n-type semiconducting regions, and no metal-semiconductor barriers. It was concluded that the photovoltaic effects measured in these specimens occurred at p-n junctions, and the device I-V characteristics were shown to be consistent with this. However, the question remained whether this was a junction between p- and n-type CdS, or between n-type CdS and some other semiconductor material (i. e., a heterojunction). The correlation between the spectral responses for the photoconductive and photovoltaic effects in CdS was felt to eliminate the need for any other type of material being active in the photovoltaic effect, since the photoconductivity was a bulk effect in the CdS, and there was no suggestion that this was in any way associated with the

presence of another semiconductor material. It was concluded that the extrinsic response must arise from transitions from an impurity band in the CdS bandgap, as suggested by Reynolds. The model proposed consisted of a junction between normal n-type CdS base material, and a region of p-type CdS having an impurity band in the forbidden energy gap, the band arising from the presence of a high density of levels in the middle of the CdS bandgap, introduced by the Cu dopant.

In 1963, Spitzer and Mead (373, 374) reported work tending to support Williams and Bube's conclusion that the extrinsic response in CdS cells arose from photoemission of electrons from a metal into the CdS. Spitzer and Mead used specimens prepared by cleaving n-type CdS crystals in an evaporant stream of metal, under high vacuum. Thus, it was felt that the contacts produced in this way should be free of contaminant effects introduced by interaction between the CdS and the atmosphere, whereas in earlier work such interactions could reasonably be expected to arise, and lead to surface states which would modify the energy band structure at the junction. Diode I-V characteristics, spectral response, and capacitance-voltage measurements, were made on the specimens. Determinations of the barrier height at the junction from these measurements were consistent and showed that the value of the barrier height was related to the work function of the metal used to form the barrier. The experiments covered a range of metals from Pt (which produced a barrier height of 0.85 eV) to Al (which produced an ohmic contact, barrier height < 0.10 eV). Some measurements were also made on specimens produced by depositing the same metals on CdS cleaved in air, and for these, much less correlation between work function and barrier height was found. This indicated the presence of surface states, which would affect the barrier height by the mechanism discussed by Bardeen, as described in Section III-D-2. The consistency of the barrier-height values measured in the vacuum-cleaved specimens suggested that the junctions produced in this way were of the metal-semiconductor type, with no intermediate region of opposite conductivity type, or of a different material. Thus, the extrinsic response must arise from photoemission, as proposed by Williams and Bube.

Further experimental evidence relevant to the debate on the mechanism of the CdS cell was presented by Palz and Ruppel in 1964 (375). Photoconductivity and photovoltage responses were both measured in the same samples, which consisted of CdS vapor-grown platelets with one ohmic In contact and one evaporated blocking contact of Te, Au, or Ag. The electrodes were 0.75 mm apart, on the same side of the crystal, and the specimen was illuminated on this same side. The crystals were high-resistivity photoconductive CdS, with a dark resistivity of 10^{14} Ohm \cdot cm. The photocurrent was measured with a 6-V applied bias, and the open-circuit photovoltage was measured without external bias. The illumination system used two light sources, one with a fixed wavelength, obtained with an optical filter, the other varied by use of a monochromator. The results showed that the photoconductivity induced by the fixed-wavelength light was quenched by the light of variable wavelength, photoconductivity minima being found for quenching light of wavelengths 9500 and 14,600 Å

regardless of the fixed-wavelength used. The converse results were found for the photovoltage measurements, the photovoltage reaching maxima for variable-wavelength light which produced photoconductivity minima, and again the wavelengths of these maxima and minima were independent of the fixed-wavelength used, though the absolute values changed for different fixed-wavelengths. These results were explained by proposing that the photoconductivity quenching and photovoltage enhancement were both caused by the freeing of holes by the variable-wavelength light. This would occur because photoconductive gain is dependent on the minority carriers being trapped (370), whereas photovoltages are generated by mobile minority carriers.

The conclusions follow the experimental results seemingly inescapably, and thus the work of Bockemuehl et al., and Palz and Ruppel, supported Reynolds' proposition that photoexcitation from intermediate energy levels existing in the forbidden band-gap formed the basic extrinsic response mechanism for CdS cells. However, the experiments were performed on crystals of a type very far removed from those used for cell manufacture, so that a strict correspondence between the two situations cannot be assumed.

The theory of photovoltaic effects which could be seen in photoconductive materials was considered by Keating (376), working from the assumption that the photo-induced minority- and majority-carrier densities were high compared with the dark concentrations. (The normal semiconductor photovoltaic theory assumes that the photo-induced majority-carrier density is small compared with the dark majority-carrier density.) The theory was first established in general terms, and then applied to heterojunctions and homojunctions in photoconductors, and to junctions between photoconductors and semiconductors. Keating then discussed the relationship between the theory and reported measurements and postulated mechanisms in CdS cells, and concluded that the most likely explanation of CdS cell operation would be based on the existence of a CdS-Cu₂S heterojunction. However, it was felt that the physical situation in the real cells was so far from the idealized junction structures analyzed in the theory that such an identification was tentative only.

With the demonstration of the success of the thin-film CdS cell by groups working at Harshaw Laboratories and Clevite Laboratories, research and development of cells intended for power generation has been concentrated on these, rather than on the single-crystal cells. Further work on the theory of CdS cells has also been done with special relevance to the thin-film CdS cells; this is dealt with in the next section of this report. However, as shown by the above account, considerable work has been done on single-crystal cells, aimed at elucidating their mechanism of operation. It will be appreciated from this account that considerable controversy exists on this subject, and no doubt research and analysis will continue for some time before a conclusion is reached.

5. Cadmium Telluride

The earliest work directed toward the use of CdTe in solar cells was that done under Signals Corps funding at RCA Laboratories, starting in 1955 (152). Since the theoretical efficiency calculations showed that the energy gap of CdTe lay close to the optimum for solar energy conversion, a major interest was taken in this material. As for most of the semiconductors investigated under this contract, suitable material was not available commercially, and consequently a good proportion of the experimental effort was put into growing crystals from which photovoltaic cells could be made. CdTe polycrystalline ingots were prepared by reacting the constituent elements in a graphite boat sealed in an evacuated quartz ampoule. The graphite boat was found necessary to avoid attack of the quartz by the melt. Gradient freezing was used to form the ingots, which were made in both conductivity types, the type being determined by the stoichiometry of the material (loss of Cd giving p-type conductivity), as well as by the presence of impurities. (This stoichiometry dependence of conductivity type is unusual, since the solid solubility of the constituent elements in a compound semiconductor is usually very low indeed, so that departures from stoichiometry result in the formation of a separate solid phase. This effect is especially pronounced in GaAs.) The CdTe initially produced was of high resistivity ($\sim 1000 \text{ Ohm} \cdot \text{cm}$), but improvements in the purity of the starting materials, and the provision of the graphite boat, enabled the resistivity to be brought down to $\sim 30 \text{ Ohm} \cdot \text{cm}$. Diffusion of Au, Ag, and Cu into the CdTe was performed from layers of these metals deposited on the crystal surface, in a sealed quartz ampoule. The results were complicated by the loss of Cd from the CdTe, causing conductivity type inversion, for diffusion temperatures above 700°C . However, by adding excess Cd to the diffusion ampoule, and by limiting the process temperatures, some photosensitive p-n junctions were prepared. These showed V_{OC} values up to 0.55 V, but the I_{SC} values were extremely small (microampere range) because of high series resistance in the devices, arising from the low conductivity of the base material.

Another early report of the photovoltaic effect in CdTe was given by Van Doorn of Philips Laboratories, Eindhoven, in 1956 (377). From the specimen preparation procedure given, it appears that the junction may have been a metal-semiconductor barrier rather than the p-n junction claimed by Van Doorn, since the contact was apparently formed by allowing AuCl_3 solution on the surface to react with the CdTe, followed by removal of the AuCl_3 by KCN. However, the spectral response results shown by Van Doorn show a good photovoltaic response with a sharp rise in V_{OC} at photon energies slightly less than 1.5 eV, corresponding to the band edge of the CdTe. These measurements were made over a range of temperatures, and were used to calculate the change in E_g with temperature.

An early Russian interest in the work was reported by Lomakina et al. (378). Cells were made on n-type polycrystalline wafers of 1 to 2 cm^2 , by diffusion of elements from Group I of the periodic table. (Specific elements used were not indicated.)

Spectral response measurements indicated an energy gap value of 1.34 eV, rather less than that reported by Van Doorn. Apparently quite reasonable diode characteristics were seen ($I_0 = 7.25 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2}$, $A = 1.65$), and the cells showed V_{oc} values of $>0.5 \text{ V}$, I_{sc} values of $2 \text{ mA} \cdot \text{cm}^{-2}$, and conversion efficiencies around 2% under $30 \text{ mW} \cdot \text{cm}^{-2}$ sunlight. Such a low illumination intensity would minimize the effects of losses due to series resistance. Further reports of this Russian work appeared in 1960 (355,379,380) showing a distinct improvement in the cell quality. These devices were made on both p- and n-type single-crystal wafers, by coating the crystal surface with suitable metallic dopants [quoted as Au in Ref. (355)], followed by heating; the remaining metal film was used as an electrical contact to the diffused region, and this film had an optical transmission of $\sim 50\%$. The I-V characteristics shown indicate good diode characteristics, with $V_{oc} = 0.65 \text{ V}$, $I_{sc} = 8 \text{ mA} \cdot \text{cm}^{-2}$, and conversion efficiencies of 4% for operation under $89 \text{ mW} \cdot \text{cm}^{-2}$ sunlight. The energy conversion performance was measured over the temperature range 110 to 380°K , the efficiency falling to about half of its room-temperature value at $\sim 100^\circ\text{C}$ (380°K). Spectral response measurements showed the expected rise at the band edge, but a good response was maintained throughout the range 4000 to 8000 \AA , indicating a shallow junction. In Reference (380), a most interesting analysis of the diode characteristic was performed, in which the departures from the diffusion theory of Shockley were discussed. The diode characteristics for deep-diffused junctions were found to fit quantitatively the Sah, Noyce, Shockley theory with recombination-generation in the space-charge region. Shallow junctions, however, were found to show a larger current than theoretically predicted at lower voltages, and this was thought to be due to tunnel current in the narrow junctions produced under these conditions. This explanation of the observed diode characteristics thus closely parallels the account given by Wolf for silicon solar cells (194). Spectral response measurements into the high-photon-energy region were made by Dubrovskii on these cells (355), and these showed that the quantum efficiency of the devices fell from the band-edge with increasing photon energy up to $\sim 4.0 \text{ eV}$, but then increased again at higher photon energies up to the limit of the measurements at $\sim 5.4 \text{ eV}$. This was ascribed to impact ionization by the carriers produced on absorption of photons with energies $h\nu > 2 \times E_g$. This work was therefore a forerunner for the results reported by Gutkin in 1965 (333), in which this same phenomenon was observed in GaAs. Further observations on the optical properties of CdTe were reported by Dubrovskii in 1961 (356), in which impurity response on the low-energy side of the band edge was seen; the results are not of importance for photovoltaic energy conversion purposes. The last report of this Russian work on CdTe solar cells appeared in 1961 (381). The cells were apparently of the same type as before, and the efficiency had been improved to 6%, with $V_{oc}=0.75 \text{ V}$, and $I_{sc} = 9.8 \text{ mA} \cdot \text{cm}^{-2}$, under solar illumination of $77 \text{ mW} \cdot \text{cm}^{-2}$; the cell area was $\sim 1 \text{ cm}^2$.

Work in the U.S. directed toward the development of single-crystal CdTe cells was performed at the Armour Research Foundation, funded by the Signals Corps, starting in 1959 (382). This work was almost entirely concerned with developing

crystal growth, purification, cutting, polishing, and etching techniques, and with investigating diffusion. Diodes were made for experimental purposes, but successful solar cells were not made.

With the demonstration of the feasibility of thin-film CdTe cells, and the start of the GE project to develop these in 1961 (described in the next section), interest in CdTe cells in the US shifted away from single-crystal work.

However, Rodot's group at CNRS, France, reported work on cells made on single-crystal CdTe (383), using the methods developed for use with thin-film cells by Cusano at GE. Cells were made on n-type single-crystal base material, In doped, by deposition of a thin layer ($\sim 1 \mu\text{m}$) of high-resistivity intrinsic CdTe by vapor deposition onto a CdTe base wafer at 300°C . This was followed by flash evaporation of a thin film of Cu_2Te , which formed a blocking contact to the semiconductor. The diode characteristics and capacitance-voltage measurements made on the cells indicated that the cells contained p-n junctions formed between the n-type base material and a surface p-region formed by copper entering the high-resistivity CdTe film, and providing an acceptor level. The band-structure proposed for the junction was closely similar to the "Mott barrier" discussed in II-C-2, as shown in Figure 65: $d = 1.6 \mu\text{m}$, $V_0 = 1.0$ to 1.3 eV , with the degenerate Cu_2Te acting as a metal. The best single-crystal cell obtained had $V_{\text{OC}} = 0.5 \text{ V}$, $I_{\text{SC}} = 14 \text{ mA}\cdot\text{cm}^{-2}$, and an efficiency of 5%, under $62\text{-mW}\cdot\text{cm}^{-2}$ tungsten light (2800°K). The nature of the junction band structure in these calls was further discussed by Rodot (384); it was concluded that this could behave either as a graded p-n junction or as a metal-semiconductor barrier, depending on the conditions of preparation.

This, then, is the current status of single-crystal CdTe cells. Efficiencies up to 6% have been seen, but these are no better than the thin-film cells made with this material. Since it is considerably easier to prepare polycrystalline thin films of CdTe suitable for photovoltaic device use than to grow single-crystal material with comparable properties, the current state of the technology discourages work on single-crystal cells.

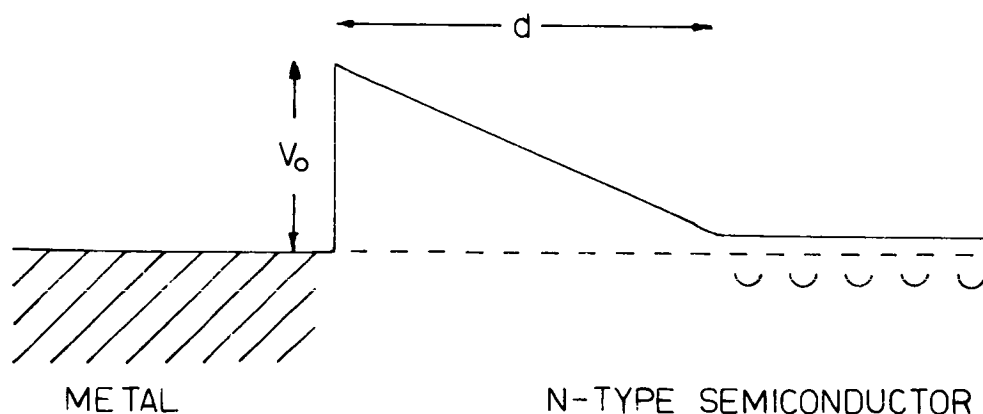


Figure 65. Band diagram of a 'Mott Barrier'

6. Other II-VI Semiconductors

Photovoltaic effects have been reported in other II-VI semiconductors, but without major effort to develop energy-conversion devices. Metal-semiconductor barriers were used to obtain photovoltages in CdSe in a series of exploratory experiments done at RCA Laboratories in 1960 (191). The CdSe crystals were grown by vapor deposition from powdered starting materials, in a sealed tube at about 1000 °C; the method was closely similar to that developed by Reynolds and others for use with CdS, as described above. Very small photocurrents were obtained, and a maximum $V_{oc} = 0.04$ V was seen. The spectral responses of the devices were measured, showing a long "tail" extending into the infrared. Because of the small photovoltaic responses seen, this work was not pursued further. Recently, however, work in the Ukraine by Komashchenko and Fedorus (385) has indicated an interest in cells made by depositing Cu_2Se barrier layers on n-type CdSe single-crystals. Under $150\text{-mW} \cdot \text{cm}^{-2}$ illumination, $V_{oc} = 300$ to 350 mV, $I_{sc} = 30 \text{ mA} \cdot \text{cm}^{-2}$, and an efficiency of 3% were obtained. In addition, cells with various metallic blocking contacts were made (Ag, Au, Cu, and Pt). Analysis of spectral response measurements showed that the cells with Cu_2Se barriers, and those with metallic barriers, all behaved as normal metal-semiconductor junctions, and the difficulties associated with explaining CdS-cells did not exist in this case.

Russian work on ZnS single-crystal cells has also recently been reported (386). The samples were prepared on wafers cut from n-type single-crystal ZnS formed by vapor deposition (presumably a development of Reynolds' method for growing CdS crystals). The junctions were formed by vacuum-evaporating a thin layer of Cu onto the crystal surface, followed by a heat treatment at 650 °C for a few minutes to cause diffusion of Cu into the ZnS. Measurements of diode characteristics and the spectral response of the photovoltaic effect showed normal results, ZnS having a wide bandgap, and thus responding only to light of wavelength less than 5000 Å. The I-V characteristics showed departures from diffusion theory, with $A \approx 2$ in the diode equation. Because of the wide bandgap ($E_g = 3.9$ eV) ZnS cannot be expected to be applicable to solar energy conversion, from theoretical efficiency considerations.

The remaining compound semiconductor in which photovoltaic effects have been observed is SiC. This material also has a large bandgap ($E_g = 2.86$ eV), and would thus not be expected to be applicable to energy conversion. The measurement of the photovoltaic effect in SiC was first reported in 1957 by Choyke and Patrick (387), who used the spectral response of p-n junctions to determine the optical bandgap of the material. Specimen preparation methods were not given. Russian work on alloyed-junction devices was reported by Kholuyanov in 1960 (388). The spectral dependence of photo-emf was measured over the temperature range 200 to 493°K, and the results were consistent with an energy gap of about

3 eV. The device sensitivity was low, and it was suggested that this was due to surface recombination. Kholuyanov pointed out that such devices might find application as UV detectors for use at high temperatures.

In 1962, Thiessen and Jungk reported observations of the photovoltaic effect in SiC illuminated with light of energy less than that corresponding to the bandgap (369). The cells were made by alloying silicon and aluminum into n-type single-crystal wafers, or silicon and antimony into p-type wafers. The spectral response measurements showed a photovoltage peak at 1.5-eV photon energy, although this was found to vary in some cells, depending on the particular crystal used. It was proposed that photoexcitation of electrons from valence to conduction band was occurring via an intermediate energy level in the forbidden band. The best response obtained showed $V_{OC} = 0.6$ V and $I_{SC} = 0.1$ mA under illumination of $7.5 \text{ mW} \cdot \text{cm}^{-2}$. The I-V curve shape was good, indicating a good fill-factor, but series resistance effects would be minimized by the low illumination intensity used for the measurement.

As mentioned initially, there is no possibility that the intrinsic photovoltaic response in SiC can be used for efficient energy conversion. However, the extrinsic response described by Thiessen and Jungk implies that this effect could be used for power generation, although there have as yet been no reports of such work. The materials difficulties with SiC are such that almost all the work has been done with alloyed junctions. These are not usually conducive to the manufacture of large-area devices, but it is not impossible to conceive solar cells made from SiC by this method, and the stability of the material may have relevance to some special applications.

7. Summary

In this section, then, a historical account has been given of the development of photovoltaic cells made from single-crystal (and in some cases polycrystalline) wafers of compound semiconductors. The present status of work with each of the cell types has been described, and it is seen that although none of the cells has exhibited a conversion efficiency or a cost-effectiveness as good as the present commercially available silicon cells, the special properties of most of the cell types offer opportunities which have not yet been fully exploited. For this reason, this field has potential which can only be realized through research. It is for this reason that the US Government agencies have actively supported and contributed to this effort in the past, and the recent increase in Soviet work in this area testifies to similar thinking elsewhere.

D. THIN-FILM SOLAR CELLS

1. Introduction

When power generation by solar cells became a practical reality in the late 1950's, it quickly became apparent that cells made with the active semiconductor material in the form of a thin layer have the potential advantages of:

- a. Low material costs, by minimization of the quantity of semiconductor material used.
- b. Low manufacturing cost, applying simpler processes by the use of polycrystalline layers, thus avoiding the need for single-crystal growth.
- c. High power-to-weight ratio, by minimization of cell thickness and hence weight per unit area.
- d. Low array cost, by the provision of large-area cells, thus minimizing the number of interconnections and assembly steps.

The practical realization of these benefits has been attempted in many ambitious research projects, a large portion of which have been funded by NASA and DoD. Limited success has yet been achieved in only a small number of cases, and a description of these, together with an account of the less successful ventures, is given in the following sections. To aid the reader in understanding the chronology of the projects funded by Government agencies in the field of thin-film solar-cell research, Table XX in Appendix III has been prepared. It should be noted that this chart does not show projects run by various research groups using financial support provided through their parent company rather than by contracts with government agencies. Thus, work during the 1956-1960 period, which was apparently all done on company funds, does not appear in Table XX.

It should be noted that the achievement of good conversion efficiencies in thin-film solar cells is not possible with all semiconductor materials. Consider the optical properties of silicon shown in Figure 66. The slow rise of the absorption constant through the energy range 1.26 - 2.3 eV implies that a considerable thickness of material is required to absorb photons and create carrier pairs. This, in turn, implies that minority carriers are required to travel a considerable distance, generally by diffusion, to reach the junction and be collected. Thin-film cells, by definition prepared with a semiconductor layer of minimized thickness (to obtain low weight per unit area, and flexibility), would not have adequate optical absorption if a material such as silicon were to be used. This anticipated effect has been measured in thin silicon cells, as described in Section IV-B-3-b above. In addition, the diffusion of minority carriers in polycrystalline material is generally not expected to be an efficient process, since both crystal defects and impurities segregate at grain boundaries

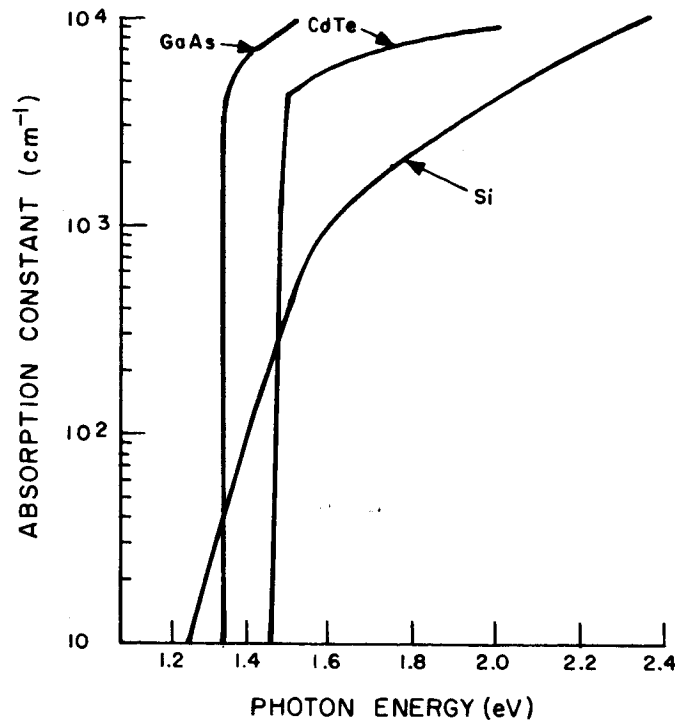
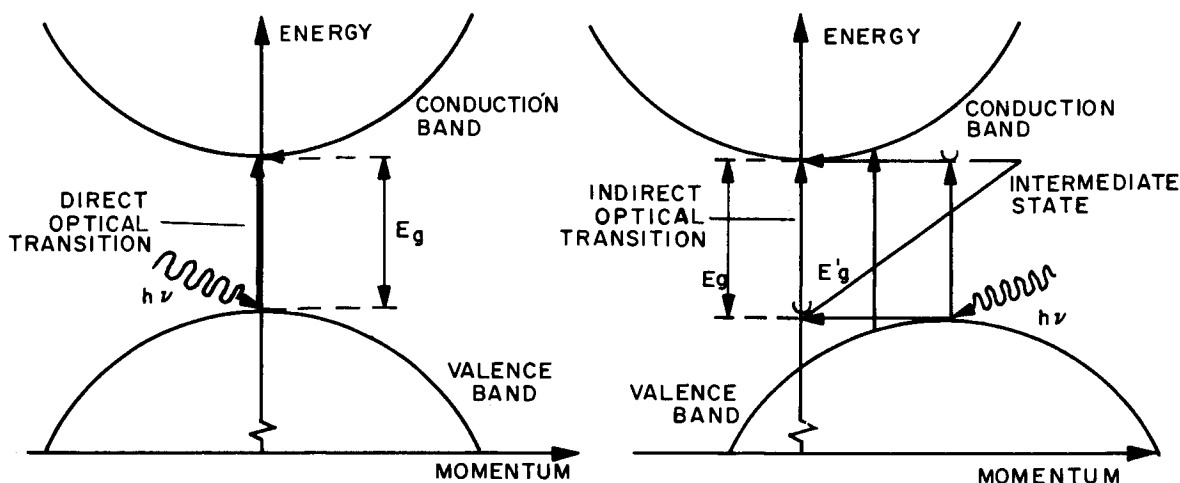


Figure 66. Optical absorption constant as a function of photon energy for direct and indirect bandgap semiconductors.

and give rise to recombination centers, through which minority carriers are lost. Practical thin-film cells are made with polycrystalline material. If the minority carriers must diffuse for a considerable distance to reach the collecting junction in such cells, the chances that they pass a grain boundary are much increased, so that low collection efficiency results. Put another way, it can be said that silicon cells require material with good carrier mobility and long minority carrier lifetime to give good efficiency. Microcrystalline silicon does not possess these properties, and thus leads to low cell efficiency, a point which has also been verified experimentally in attempts to make low-cost silicon solar cells, as described in Section IV-B-3-a above.

However, a material whose optical absorption constant is high for all wavelengths shorter than the band edge will not suffer from these difficulties. Semiconductors with the steep absorption edge shape, such as GaAs and CdTe (see Figure 66), have an energy band structure such that photons with energy close to the bandgap energy can transfer an electron from the top of the valence band to the bottom of the conduction band without the involvement of an intermediate level or a third "particle," such as a phonon. To understand this effect, it is useful to consider a graph in which electron energy is plotted as a function of electron momentum, as in Figure 67. In so-called "direct" semiconductors such as GaAs and CdTe, the momentum of an electron at the maximum of the valence band has the same value as at the minimum of the conduction band, whereas in an "indirect" semiconductor such as Si, these momentum values



a. Direct bandgap semiconductors.

b. Indirect bandgap semiconductors.

Figure 67. Simplified band structures and optical transitions.

differ. For a more detailed account of band structures, and a review of the underlying theory, the reader is referred to Bube's book (370), Chapter 7. Referring to Figure 67a, it will be seen that in direct bandgap semiconductors, absorption of a photon of energy E_g can be accomplished directly with conservation of momentum. In an indirect bandgap material, absorption of a photon of energy E_g can only be accomplished with a change of electron momentum, and hence a third "particle" must be involved in the photon-electron interaction process, to conserve momentum. Thus a photon incident on a semiconductor may have to travel a considerable distance through the material before it encounters an electron suitably associated with a third "particle" to allow the optical excitation process to occur. Referring again to Figure 67b, it will be observed that as the energy of the incoming photons increases beyond E_g , electron transitions between points other than the valence band maximum and conduction band minimum become possible. Thus, with increasing photon energy, the possible transitions require progressively smaller momentum changes, and thus the distance travelled by a photon before encountering an electron in a suitable momentum state becomes smaller, i.e., as the photon energy increases beyond E_g , so will the optical absorption constant. Other things being equal, the photon energy must have a value E'_g before the optical absorption constant in the indirect semiconductor reaches a value equal to that corresponding to photons of energy E_g in the direct semiconductor, as shown in Figure 67b.

Taken in conjunction with the theoretical analyses of conversion efficiency as a function of semiconductor energy gap, this explains why GaAs and CdTe were picked as likely materials for thin-film solar cells. The outstanding position of CdS as a base material, however, shows that the best results are not always found in expected ways, and exemplifies the statement made in the introduction that directing work only along paths which are signposted clearly by existing theories and known data will exclude discovery of unexpected results which can spring only from broader, more or less "free-wheeling" research efforts.

Radiation effects in thin-film cells have been reviewed by Loferski (390). It has been anticipated by many workers that thin-film cells will exhibit more resistance to penetrating radiation than bulk cells, and indeed this has been one of the primary justifications for the development of this type of cell. This expectation is based on the fact that thin-film cells will, by their nature, have a very thin region from which minority carriers are collected. This region may, in fact, be restricted to the depletion region of the active junction. This implies that long minority carrier diffusion lengths are not necessary, and, coupled with the fact that the effect of radiation is primarily to reduce diffusion length, should result in low radiation sensitivity. This also implies that particles which lose most of their energy inside the thin active region near the cell surface will be more effective for radiation damage than those which penetrate deeply into the cell. The depth of the region over which a particle does its damage is determined by the nature of the particle (electron, proton, alpha, or gamma), and by its energy. Only protons and electrons have been found to exist in near earth space in numbers sufficient to cause appreciable damage in solar cells. The electrons have generally greater penetrating power, and thus cause damage over a much greater depth in the cell, whereas the damage done by low-energy protons is comparatively localized in the surface region. As a rule, the higher the energy of a particle of a given type, the greater is its penetration into the cell. Thus one might expect low-energy electrons to cause damage localized near the surface of the cell. However, there is a threshold of energy below which electrons cannot transfer sufficient energy to an atom in a semiconductor lattice to cause a displacement which gives rise to radiation damage. Thus, electrons will not be expected to have much effect on the semiconductor in thin-film cells, whereas low-energy protons can cause a greater effect. However, the low-energy electrons can affect the optical properties of a covering plastic, if this is used in the cell construction. The experimental evidence on radiation resistance of thin-film cells is still sparse, but it does in general bear out the picture given above. Data on specific cell types are reviewed in the appropriate sections forming the remainder of this chapter.

The thin-film solar-cell field enjoys frequent review papers. General surveys of progress at various times during the period 1959-1967 will be found in references 287, 247, 254, and 391 through 395.

2. Cadmium Sulfide

The discovery of the photovoltaic effect in CdS was made by Reynolds in 1954, and early work aimed at exploiting the phenomenon was done by groups working under Reynolds, at the Harshaw, Clevite, and Eagle-Picher laboratories: this phase has been described in Section IV-C-4 above. Initial work on thin-film CdS cells quickly followed the original single-crystal work, and the subsequent development has been reviewed recently by Shirland (357). The account given below for the period 1954-1958 is drawn from this source.

The earliest report of the observation of a photovoltage in a thin film of CdS was by Nadjakov et al. (396) in 1954, who used a CdS film vacuum deposited over a pair of aluminum and gold contacts, a small photocurrent (10^{-8} - 10^{-9} A) being obtained under illumination. A program aimed specifically at investigating the feasibility of solar cells made from CdS films was run at Clevite laboratories during 1954 (397), and thin-film cell work was also supported there by the USAF during 1955-1956 (398). Conducting glass and copper substrates were used, with a rectifying contact made with copper, Cu_2O , or Cu_2S : photocurrents in the 10^{-5} - 10^{-6} A range were obtained, thus demonstrating that the concept was feasible in principle. Another attempt to apply Reynold's cell fabrication method to a thin-film device was made by Cabannes in 1958 (399). CdS was deposited under vacuum onto semi-transparent films of Cu or Au on glass substrates, with an In ohmic contact being deposited onto the CdS film. Again, photocurrents in the tens of microamperes range were seen and, as with the Clevite cells, the efficiencies were limited by high internal cell resistance.

This resistance problem was tackled by Gorski at Harshaw Laboratories during 1960, who managed to evolve a process for vacuum deposition of thicker CdS films (Cabannes had found that films thicker than $2\text{ }\mu\text{m}$ cracked off the substrate). The same processing methods as developed for making active junctions in the single-crystal CdS cells were used. In these, a layer of fine copper particles was formed on the CdS surface by electro-deposition, followed by a heat treatment to form a Cu-CdS junction.

In the same year (1960), Moss of RCA Laboratories reported results obtained with cells made from vacuum-evaporated CdS layers (400), but using a different junction-forming technique. Finding that the copper electro-deposition process led to uneven results with polycrystalline CdS layers, the RCA workers applied a paste of finely-divided metallic copper to the CdS surface, either by brushing or by silk-screening. This was then followed by a heat-treatment to form the Cu-CdS junction, as for the Harshaw process. Both groups used glass substrates with the CdS applied to a transparent conducting coating of tin oxide, the completed cells being of the backwall type, and having the structure shown diagrammatically in cross-section in Figure 68. The Harshaw cells showed efficiencies up to 3.5% for cells of 2 cm^2 area, whereas the RCA cells were limited by internal series resistance, with efficiencies up to 1%, on smaller areas. These results generated fresh interest in this type of cell, and several groups became involved in attempts to develop a practical cell manufacturing technique.

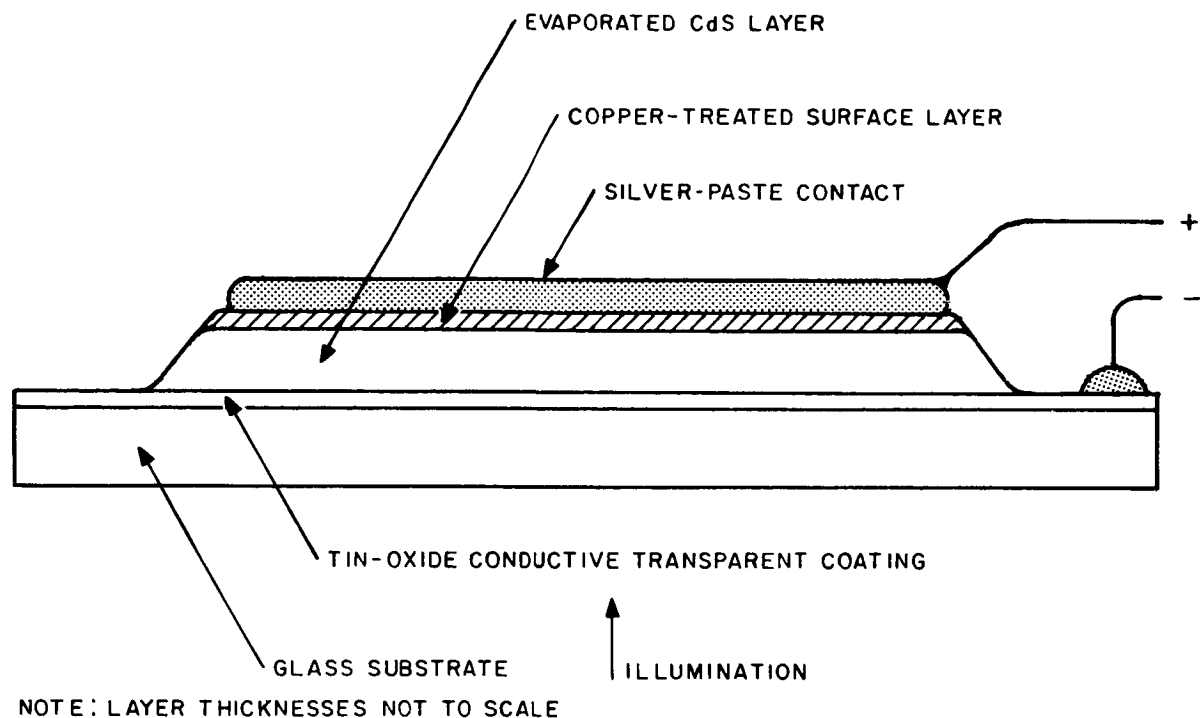


Figure 68. Cross-section of early RCA thin-film CdS cell.

In 1961, an appreciable part of the contractual effort under the USAF funding for CdS cell work at Harshaw Laboratories (401) was devoted to thin-film cells. This work was done with backwall cells, mainly on conducting glass substrates. However, several types of alternative substrate were tried, including 2 mil ribbon glass with tin oxide coating, molybdenum and tantalum metal foils, plastic films (Mylar and Teflon), and various composites (glass paper, and a Teflon-glass paper laminate). The strains in the thin glass sheets were found to be too great to allow high temperature processing or normal handling, and the plastics and laminates were found to either melt or cause unsuitable CdS film textures. However, the metal foil substrates were found to be satisfactory, and came into general use. The active junctions in these cells were made by the techniques developed for backwall cells, in which a "mossy" metallic copper layer was electro-deposited on the exposed CdS surface by plating in a solution containing HNO_3 , followed by a heat treatment cycle, and the subsequent removal of the remaining Cu by wiping the surface. The counter-electrode to the active surface was formed by applying stripes of silver paste with a ruling pen, to provide a comb-like pattern. These methods were adaptations to the frontwall cell of techniques used for the backwall cell, and hence were not ideally suited to the devices being made, which showed efficiencies of about 1%. However, the cells made in this way indicated the feasibility of the flexible substrate cell, and it remained for future work to develop cell fabrication processes better-suited to the frontwall configuration.

At this time also, lamination of cells between plastic sheets to provide protection and facilitate cell connection into arrays, was first investigated. The process involved heating and applying pressure to a sandwich built up of the foil-substrate cell and thermoplastic films, together with layers of release agents (to prevent the thermoplastics from sticking to the die). For arrays, electrical connections between cells were made by including conducting foil strips in the sandwich. Various thermoplastics were used, the more successful being polyethylene, polyethylene-coated Mylar, polytrifluorochlorethylene ('Kel-F'), and polyvinyl fluoride ('Tedlar'). Large area cells were made at this time (about 250 working 1" x 3" cells, and 85 3" x 3" cells, were made on Mo substrates during this contract), and thus the feasibility of large-area cells was immediately demonstrated. It remained for the future to pull together the good efficiencies of the backwall cells made on the conducting glass, and the large areas on a practical substrate of the metal-foil cells. This work at Harshaw also appears to have been the first occasion on which the electroless copper-deposition process was mentioned. Although the cell efficiencies resulting from its use during this period were very low, it has since become the standard method for making the Cu₂Se barrier on the CdS and will be described later. This work also showed that the active barrier layer was Cu₂Se, the evidence being based on X-ray diffraction and chemical analysis. Results also showed that the presence of cuprous ions (rather than cupric) in the electroless plating solution was essential.

The group at RCA also continued work on CdS film cells under the sponsorship of the USAF, and described their results in a series of reports during 1961 and 1962 (402). During this period, cell efficiencies were improved along with cell area, so that by the end of the contract, cells with the following areas and efficiencies had been made:

Efficiency (%)	Area (cm ²)
5.7	0.2
3.32	3.33
2.24	17.2
1.2	100 (4" x 4")

The efficiencies obtained by the Harshaw and RCA groups for backwall cells on tin-oxide coated glass substrates, thus appear to have been comparable at this time (1962). Whereas the Harshaw group had not found a suitable plastic substrate, the RCA workers obtained from a Dupont pilot line a sample of a high-temperature plastic film which proved suitable for cell fabrication. The material was a poly-imide,¹⁵ later marketed under the trade names H-film or Kapton, and now the standard plastic substrate material. The optical transmission of this plastic permits operation as a backwall cell. The original RCA work used a substrate coating of vacuum-deposited layers of chromium and gold to provide contact to the CdS film. Both backwall and frontwall cells

¹⁵ A polymer containing the ring structure: $\begin{array}{c} \diagup \text{N} - \text{C} \\ \text{C} \quad \quad | \\ \diagdown \text{N} - \text{C} \end{array}$

were fabricated, the substrate coatings being made sufficiently thin to allow reasonable optical transmission in the backwall cells, as shown schematically in Figure 69. For these plastic-substrate cells, the CdS deposition and barrier formation processes were essentially the same as those described by Moss (see above). However, the cell efficiencies were lower (about 1%) than for cells made on glass substrates.

By 1962, then, all the major elements which have led to the present success of CdS thin-film cells had been introduced:

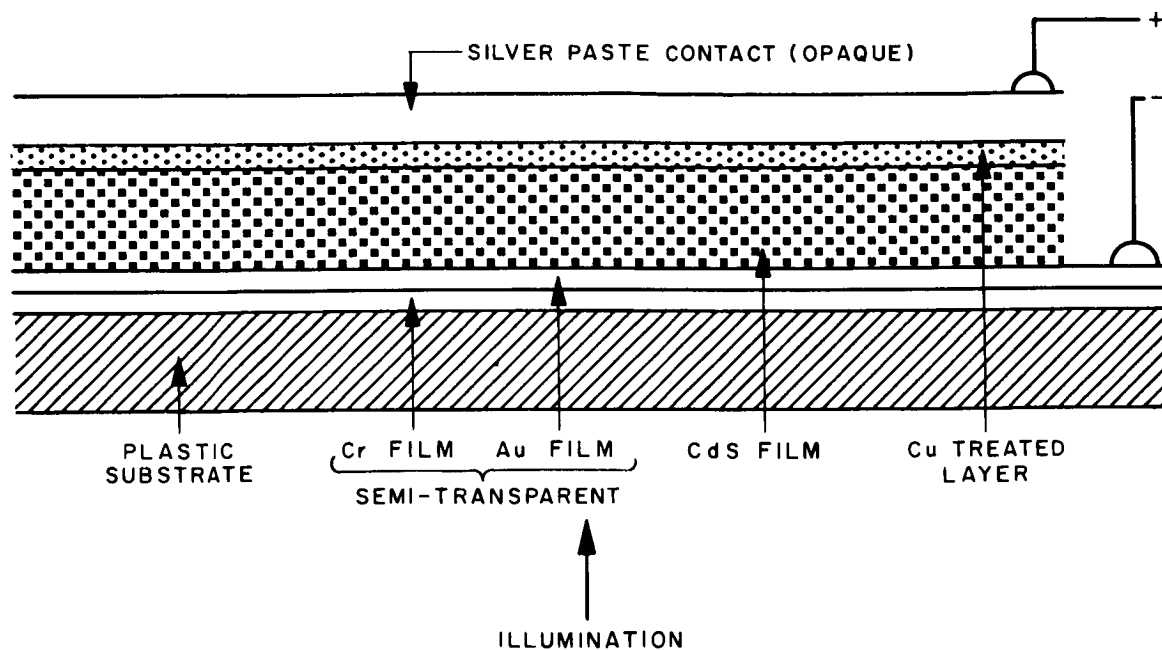
- a. For small-area ($\sim 1 \text{ cm}^2$) cells on glass substrates, encouraging efficiencies had been obtained, above 5%.
- b. For large-area ($50\text{-}100 \text{ cm}^2$) cells on glass substrates, feasibility had been demonstrated, with conversion efficiencies a little over 1%.
- c. For flexible, light-weight cells, the feasibility of metal foil or plastic film substrates had been demonstrated, with efficiencies up to about 1%.

Problems outstanding at this time were:

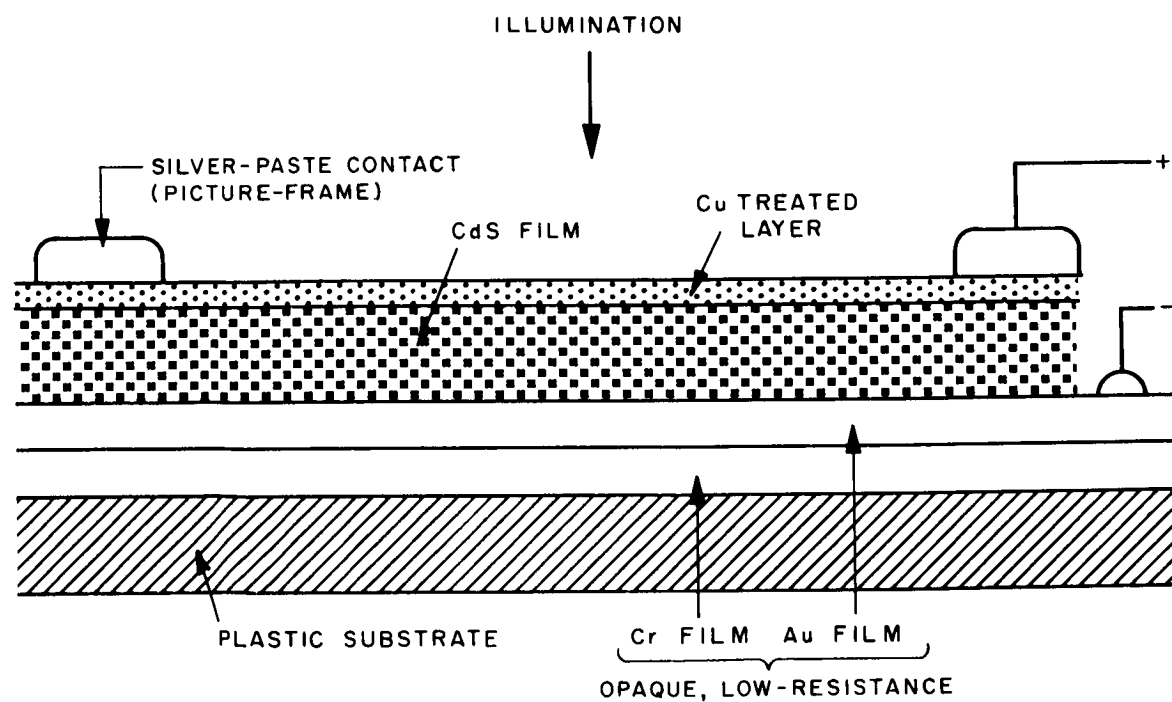
- a. The low efficiency of the large-area cells, a primary cause being high series resistance.
- b. The degradation of cell efficiency during storage, apparently because of the action of moisture from the atmosphere on the CdS.
- c. A general lack of reproducibility, particularly in the process for forming the active layer on the CdS, and in providing satisfactory electrical contact to the active surface of the CdS.

In reference to this last item, it is perhaps worth noting a fact which appears to have not been explicitly described in the reports on CdS cell work. The only way yet firmly proven to make reasonably satisfactory contact to the copper-treated surface of the CdS is to attach a metal mesh by pressure contact or use a conducting adhesive such as silver-loaded cellulose lacquer or gold-loaded epoxy. Ideally, evaporated metal contacts to this surface would be used, as in silicon cell technology. Although many attempts to develop such a process have been made (starting during the initial work described above), in no case has a reproducible technique been found. A strange fact is that occasionally working cells have been made with evaporated grids. In every reported case, however, further application of an apparently identical process has resulted in short-circuited cells. This, therefore, represents a particular example of the lack of reproducibility mentioned.

It will be understood that a large number of abortive investigations aimed at discovering ways to make improved cells had been made up to 1962. It would be inappropriate to discuss these exhaustively here, but two particular areas are worth mentioning.



a. Backwall cell.



b. Frontwall cell.

Figure 69. Cross-sections of early plastic-substrate thin-film CdS cells.

The first of these concerns the quality of the CdS layers. It was felt that increase of crystallite size should improve cell performance by reducing the number of grain boundaries in the cell (thus improving the minority carrier mobility and hence, the collection efficiency and short-circuit current). A recrystallization process employing silver for treating CdS to increase grain size was developed by Gilles and Van Cakenberghe (403), and this process was applied to the CdS layers used for cell fabrication by the RCA group (402). Although improvement in carrier mobility was seen, all operating cells made with these recrystallized layers showed low efficiencies, due partly to shorting of the active junction by silver precipitation, and partly to non-uniform barrier formation with the recrystallized CdS.

The second area of endeavor which yielded negative results concerned the barrier formation process. Ideally, this would be a vacuum evaporation step, to follow the CdS vacuum deposition, and followed, in turn, by a vacuum-evaporated contact grid. Many different elements and compounds were investigated for barrier formation, but in no case was a cell obtained approaching the quality of those which could be made by the "wet" processes originally developed.

The problem of series resistance in the large-area cells was largely eliminated by the use of metal mesh counter-electrodes applied with adhesive to the active surfaces of frontwall cells. This solution was first arrived at by Griffin of the Harshaw group, who used an electroformed mesh with 85% optical transmission but very closely spaced grid lines (about 70 lines per inch). This was attached to the cell surface by lamination with transparent plastic as described above, the mesh-Cu₂S contact being mechanical only. Other groups developed similar techniques shortly afterwards (e.g., the RCA group used gold meshes, which in experimental cells were attached by pressure-sensitive adhesive tapes, a particularly quick and convenient process).

Testing revealed stability problems which were not easily solved, however. It now appears that effects from two causes were seen, although this was not clearly evident at the time:

- a. Shelf degradation, apparently by interaction of moisture with the CdS, and a familiar problem from the start of work on CdS cells, was present.
- b. In addition, a degradation caused by temperature cycling of cells with laminated grids appeared. This was manifested by short-circuits developing in the cells, or by an increase in cell series resistance, after about 20 temperature cycles intended to simulate satellite orbit conditions.

The solution of these problems has not been quick or easy, and this will be described later.

In slight digression, a project will be described which ran at the National Cash Register Corp. Laboratories starting in 1962, under funding from the USAF. The objective of

this project was to develop an alternative CdS film manufacturing process. It ran until the middle of 1965, with progress reports being published periodically (404-406). A spray technique was developed for making CdS films based on pyrolytic decomposition on a heated substrate of organic materials containing cadmium and sulfur. Layers were made from aqueous solutions of cadmium thiocyanate $\text{Cd}(\text{SCN})_2$ and the complex formed by cadmium chloride and thiourea $\text{Cd}[(\text{NH}_2)_2\text{CS}]_2\text{Cl}_2$. Typically, the substrate was positioned on a hotplate below a sprayhead (of the type used for forming aerosols of paint), with the substrate at about 200°C . The spray solution was applied in a rather dilute form, and careful filtering to remove gross particles, and substrate motion to maintain uniformity of deposition and adequate temperature control, were found to be necessary: the original reports list process details and precautions.

Substrate selection proved a major problem. Initially, cells were made on conducting glass, as was used for the vacuum-evaporated CdS films. The cells made were of the backwall type, and efficiencies up to 3.5% were obtained on 2 cm^2 devices containing Cu_2S barrier layers formed by a spray process similar to that used for the CdS deposition. A suitable solution for this process was found to be a mixture of aqueous solutions of copper acetate and N-N, dimethyl thiourea. With frontwall cells on flexible metal substrates, however, difficulties in obtaining good cell efficiencies were encountered. Substrates investigated were molybdenum, cadmium-plated copper, phosphor-bronze, various steels, and, during the second contract period, a Cu/Cd-alloy plated steel.

Results from this work showed that large-area cells ($3'' \times 3''$) on metal foil substrates, could be made with conversion efficiencies up to 0.56%, and that smaller cells (1 cm^2) could be fabricated with efficiencies up to 2%. In no case, however, were results obtained which were comparable to those seen in the cells made on metal substrates by the vacuum-deposition process. Since the devices produced by the spray process on glass (backwall cells) were comparable in efficiency with those produced with vacuum-deposited CdS, this result was disappointing, and the possible reasons for it are of relevance to the purposes of this review. It appears that the Cu_2S layer in these cells was considerably thicker than that used in the vacuum-process cells. Unfortunately, the barrier-formation methods for the latter do not produce working cells when the CdS layers are too thin, and the difference in thickness of the CdS in the two types of cell ($\sim 15\text{--}20\text{ }\mu\text{m}$ for the vacuum deposited CdS, $\sim 1\text{ }\mu\text{m}$ for the sprayed CdS) apparently prevents the use of the chemiplating or electroplating methods for forming the barrier layer. The thickness of the sprayed CdS layers could apparently not be increased without causing flaking of the layer from the substrate.

These sprayed CdS cells exhibited in some instances a type of behavior not seen in any other CdS cells. As described in Section IV-C-4 above, single-crystal CdS cells exhibit an extrinsic spectral response, and open-circuit voltage values, which would be appropriate to a material with an energy gap $E_g \sim 1.2\text{ eV}$ rather than the 2.4 eV of CdS. The same behavior is generally seen in thin-film CdS cells (407). However, some of the sprayed CdS cells showed a very small extrinsic spectral response, and

had open-circuit voltage values around 1.0 V. The cells thus behaved more nearly as one would expect for CdS, and this is unique among CdS solar cells. The spectral response of a high-voltage CdS cell is compared with a typical CdS cell response in Figure 70. It should be noted that the measurement conditions were not identical for these curves; however, white bias light would not be expected to appreciably alter the intrinsic response. The NCR group postulated that the response arose from a combination of intrinsic absorption in the CdS, and absorption in CuS to provide the response on the long wavelength side of the response curve. They found that the incorporation of copper into the CdS film appreciably increased the extrinsic response of cells which otherwise would show mainly intrinsic response, but the quantities of copper required were appreciable (up to a ratio of 1:20 Cu:Cd in the spray solution). High-voltage cells showed efficiencies up to 2%, but were severely series resistance limited. A positive correlation between V_{oc} and R_s was found, and in spite of the feeling of the NCR group that this series resistance did not pose an unsolvable problem, it certainly contributed to the difficulties in making good cells of this type. For cells with V_{oc} values between 0.8 and 1.0 V, R_s values for un-illuminated cells lay between 150 Ohm and over 100 kOhm, and although R_s values usually decrease under illumination in CdS cells, low values of I_{sc} (between 0.015 and 1.5 mA. cm⁻²), and F (between 0.4 and 0.25) were in general obtained on these cells.

In summary, then, the NCR work proved the feasibility of a potentially low-cost method for making CdS thin-film cells, but the efficiencies of the cells made in this way were felt to be too low to justify continued efforts on this process for the provision of solar cells for space power.

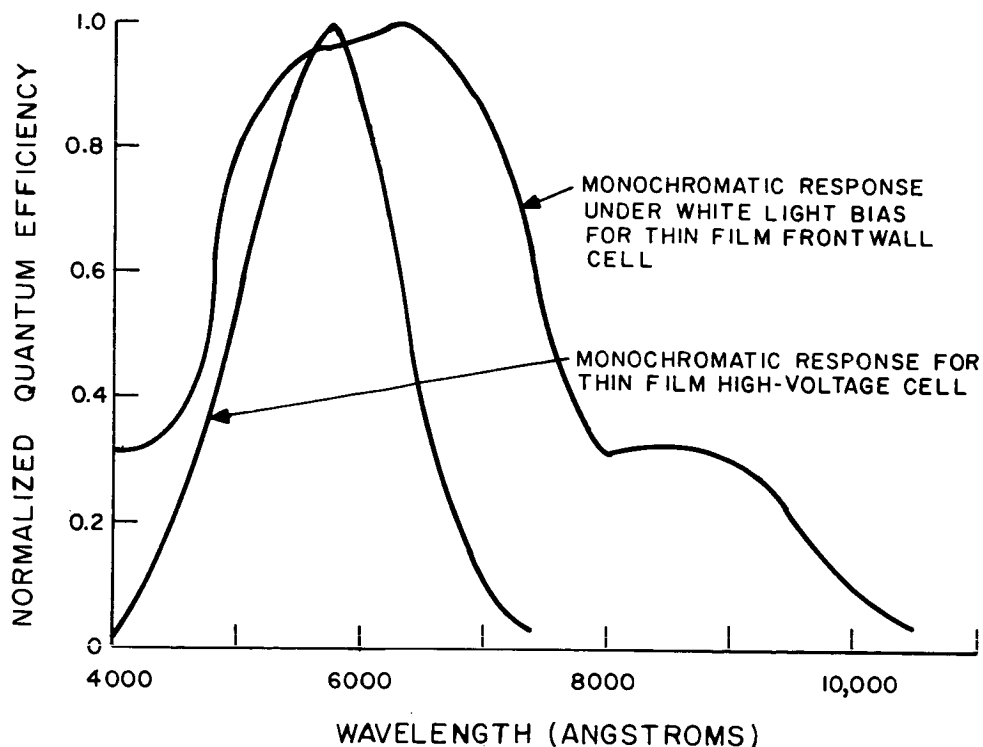


Figure 70. Curves comparing spectral responses of normal (extrinsic) CdS cells, and chemically sprayed (intrinsic) CdS thin-film cells.

Meanwhile, the work on CdS thin-film cells at Harshaw Laboratories, described above, continued. The original contract (401) was succeeded by a second (408), also funded by the Air Force, while an additional project was funded by the National Aeronautics and Space Administration, both being carried out in the same laboratory (409). Under the Air Force contract, the attachment of the grids to the Cu_2S layer by lamination, first used near the end of the previous contract (401), was developed further. The thermoplastic then used was a nylon film (trade-name "Capran"), with outer lamination sheets of Mylar, to give a cell cross-section as shown in Figure 71. Contact to the grid mesh was by a metal foil tab, also attached during lamination. Various materials were evaluated for the grid mesh (gold, silver, copper, and nickel), and best results were obtained with the gold mesh, which was then used for most of the cells. It was also discovered about this time the Mylar, although adequately resistant to particle radiation, darkened under UV exposure. The use of a Mylar film coated with a UV-absorbing layer was found compatible with the lamination process after modification, although various other plastic films, including Kel-F, Teflon (poly-tetrafluoroethylene), polypropylene, and Phenoxy-8, were tried and rejected.

A pilot line for cell production was started at this time, fabricating cells by the following process:

- a. 2-mil molybdenum foil substrate was cleaned and etched, and a 2-mil layer of CdS was deposited under vacuum onto the heated substrate.

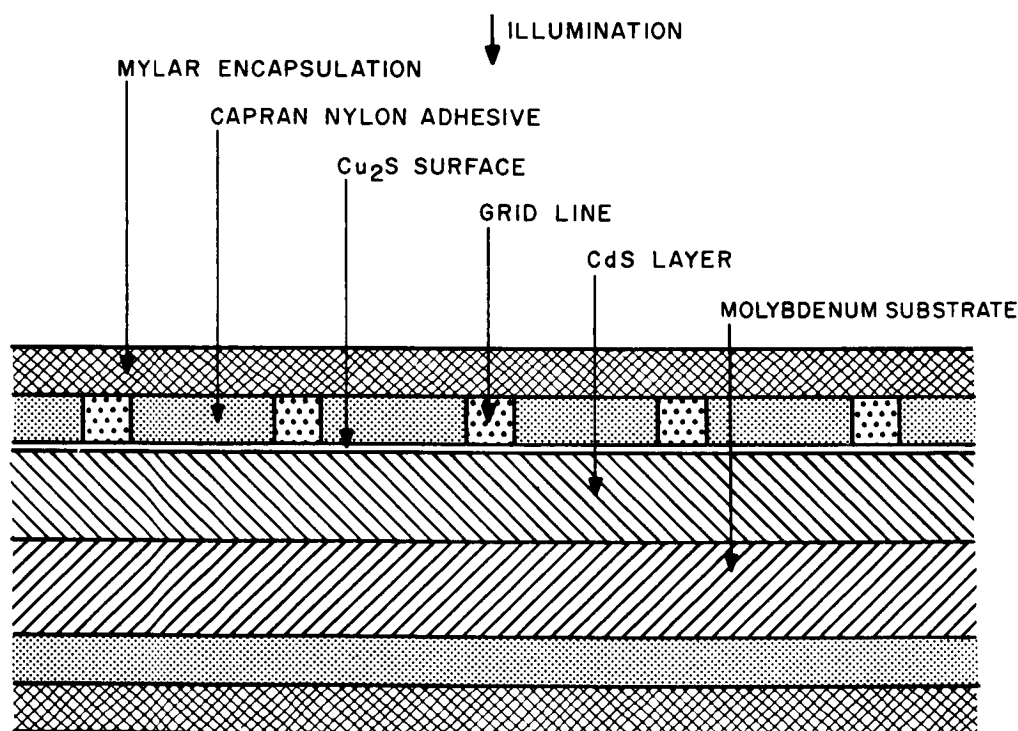


Figure 71. Cross-section of Harshaw thin-film CdS cell, showing encapsulation and grid attachment by nylon/Mylar lamination process.

- b. "Mossy" copper was electrodeposited on the CdS surface from an acid solution (HNO_3), followed by a heat treatment in air ($\sim 250^\circ\text{C}$ for a few minutes) to form the copper-activated surface. Excess copper was wiped off either before or after the heat treatment.
- c. The cell was laminated with gold mesh, nylon, Mylar, and connector tabs.

It should be noted that increasing commercial interest in the cells became apparent at this time, so that precise process details become more difficult to glean from the reports.

More than 1500 (3" x 3") cells were made on the pilot line, with efficiencies averaging 2.2%, and the highest efficiency seen was 5.12%.

Other research on cell processing was performed, aimed at discovering alternative cell fabrication methods or at elucidating the mechanisms of the established processes. In particular, other ways of depositing the CdS layers were tried, presumably prompted by the NCR sprayed-CdS work. Electrophoretic deposition of CdS was used in which colloidal CdS particles, charged by interaction with a suitable fluid suspension medium, were deposited by application of a d-c potential to the substrate, followed by sintering to provide compaction and adhesion to the substrate. Satisfactory adhesion and grain size could not be obtained. A technique in which a water suspension consisting of a mixture of CdS and CdCl_2 was sprayed onto a heated substrate was also investigated, but was not found satisfactory.

Studies of the CdS film structure were also pursued, and a considerable effort was made to develop a model of cell operation from spectral response studies. The resulting one-trap mechanism for cell operation was later rejected by the same group; the reader is referred to the original reports for a more detailed account of this.

In the parallel work under NASA support, similar cell fabrication processes were generally used, and numerous 3" x 3" cells were made, with efficiencies in the 2.5 to 3.5% range. In addition, 16 (6" x 6") cells were prepared, with unstated efficiencies, although it was implied that these were not greatly lower than those of the 3" x 3" cells. A feasibility study was run to determine the economics of manufacture of the 3" x 3" cells, and various alternatives in terms of quantities and production rates were analyzed, resulting in projected costs of \$65 to \$70 per watt.

Alternative metal foils for substrates were investigated, including tungsten, niobium, zirconium, titanium, and kovar, but in no case were efficiencies obtained better than those with molybdenum, although titanium-substrate cells offered potential weight-saving advantages. Pressed mesh grids were used, and electroplated grids were also investigated, using a photoresist pattern on the CdS surface, and plating through the windows developed in the photoresist. Attempts were also made to use vacuum-evaporated grids, with wholly negative results.

In 1962, Clevite Research Laboratories also obtained support from NASA for CdS thin-film cell research (410). Work in this area had apparently been in progress prior to this time, presumably supported by internal funds. An account of the results achieved by Clevite during the period 1956-1962 has not been located. However, the first quarterly report under NAS7-203 indicates that the group was working with glass, copper foil, and H-film substrates. The active barrier was being made by the electrodeposited-copper process, but an alternative technique was also tried, involving the spraying of Cu_2O onto the surface of the CdS. 4" x 4" cells were being made, but the results obtained with cells on plastic substrate and with cells made by the sprayed- Cu_2O technique were not encouraging, their efficiencies being less than 1%. However, because of its potential for making backwall cells, work with H-film and glass substrate cells was continued, and eventually cells on glass with efficiencies up to 4% in the 4" x 4" size were obtained. These backwall Clevite cells were prepared on substrates without a conductive coating, the CdS being given a thickness and conductivity adequate to allow lateral conduction to a "picture-frame" electrode at the cell periphery. However, CdS films with sufficient thickness would not adhere adequately to the plastic substrates, so that 6 cm^2 cells on plastic substrates had efficiencies of about 2.5%, being partly limited by series resistance.

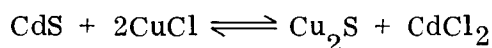
During 1964, then, the Harshaw and Clevite cells were both made with vacuum-deposited CdS films, using the electro-deposited copper process for forming the cell barrier. However, Harshaw cells were frontwall devices on metal (molybdenum) substrates, whereas the Clevite cells were of the backwall type, on polyimide substrates. Early in 1964, F. A. Shirland left Harshaw and joined the Clevite group of Augustine and Deshotels. Both the Harshaw and Clevite groups obtained continued funding for CdS cell research (see Table XX) under contracts with NASA and USAF, but Shirland noted (357) that at least Clevite also provided internal support for the research. Both groups addressed themselves to the problems of obtaining:

- a. Efficient cells on lightweight flexible substrates,
- b. Process control to give good production uniformity, and
- c. A solution for the cell stability problem.

The Harshaw group continued to use molybdenum substrates, and developed a method for reducing the thickness of these from 2 to 0.3 mils by etching after cell formation thus avoiding the difficulties of handling very thin foil (411, 412). This process largely negated the weight advantage of the plastic films, although it would probably be difficult to incorporate such a process into a manufacturing line at low cost. However, for a single cell, a power-to-weight ratio of 77 watts lb^{-1} was achieved using this technique in early 1965. During this period, also, the Harshaw group moved toward the use of electroplated grids, rather than the application of electroformed meshes. This process could also provide weight-saving advantages. The Harshaw group re-investigated the use of laminated Mylar as an encapsulant, and found that under UV

exposure equivalent to one year in earth orbit almost complete darkening of the plastic occurred, with complete loss of output from cells with this encapsulant. Cells laminated with Kapton showed degradation under the same orbital simulation, but this was felt to be due almost wholly to thermal effects, as darkening of the Kapton was not seen. However, this material was found to exhibit optical absorption towards the blue end of the cell response spectrum, so that initial output from Kapton-coated cells would always be at least 20% less than from Mylar-coated devices. Proton and electron radiation damage experiments showed the cells to be more radiation resistant than n/p silicon cells. A novel cell fabrication method was tried, in which CdS was deposited on copper substrates, and processed to form a backwall cell by diffusion of copper into the CdS: this was found not to give promising results.

In late 1963 or early 1964, a major advance in cell fabrication methods had occurred. This was the "chemiplating" method for barrier formation, which is now commonly used, albeit with some improvements. The CdS layer (on its substrate) is dipped for a period of a few seconds into a suspension of CuCl in water at 90-100°C and then rinsed. This is followed by a heat treatment, in which the cell is held at approximately 250°C for about 2 minutes. The CuCl suspension must be prepared with cuprous chloride from which cupric ions have been removed by leaching the powder in HCl, after which processing the CuCl should be stored in darkness, to prevent the formation of further cupric ions by oxidation of the CuCl. The process is known to form a layer of cuprous sulfide (Cu₂S) on the cell surface, probably by the ion-exchange reaction:



The brief heat-treatment following the dip is believed to allow the diffusion of cuprous ions into the CdS, in association with chloride ions, to form a narrow surface region of CdS doped with these ions. This latter point is still not conclusively established, however.

Although this procedure was first used for the fabrication of solar cells by the Harshaw group (411), an analogous process had been described in 1962 by Cusano (413). This was used to make photovoltaic Cu₂Te/CdTe junctions, and the same author referred to earlier unpublished work by himself in which photovoltaic Cu₂S/CdS junctions had been formed by the CuCl hot dip process.

During 1964, the barrier-formation process in use at Clevite involved the application of a cuprous oxide suspension in water to the CdS film surface with a brush, the cell being at a temperature of 90-100°C (414). When a complete coating had been obtained, the cell was allowed to dry, the excess Cu₂O was wiped off, and the cell was heated to about 200°C for a few minutes. As mentioned above, these cells were of the backwall type, and were made on glass and on polyimide substrates. They showed efficiencies of 4% for cells on glass, and 2.5% for cells on plastic.

By 1965, however, the Clevite group had also gone over to the use of the cuprous chloride dip process (415), and a striking improvement in cell efficiency was obtained (416-418). The Clevite group also investigated the use of alternative halides in place of chlorine for the barrier formation process. Although the original intention was to obtain an improvement in cell stability, it happened that the most efficient thin-film cells were obtained during these experiments. Although only a limited number of cells was made, there was a strong indication that the replacement of the HCl by HBr or HI for the pre-barrier etch step was the principal factor in the change, having a larger effect on cell efficiency than the use of CuBr in place of CuCl for the dip solution. The highest efficiency seen, 8.35%, was for a cell made by etching the CdS film in HBr, then forming the barrier by the usual CuCl dip. However, the high cell outputs were maintained for only a few hours, while the cell efficiencies eventually dropped to the values normally obtained with the HCl/CuCl treatment.¹⁶ Clevite cells were now being made on metal (molybdenum) and on plastic (polyimide) substrates, both in front-wall configuration. Electroformed mesh collector grids were used, attached either by the nylon-Mylar lamination process, or by use of silver-loaded conducting adhesive. Average efficiencies were 5% for the 3" x 3" (50 cm²) device, with the best efficiency seen as high as 8.35% in a 12.1 cm² cell.

The design of the 3" x 3" cells was considerably improved over the earlier versions. The quality of the vacuum deposited CdS layers was better than before, so that thinner films could be used without short circuits being developed during barrier formation or grid application. This was presumably the result of improved substrate preparation and deposition techniques, leading to elimination of pinholes in the CdS layer. CdS layer thicknesses were now around 20 μ m, compared to the 50 μ m two years earlier. Also, the cell contacting methods were improved, the electrical leads now being integral extensions of substrate and grid instead of separate metal foil tabs attached during lamination.

Alternatives to the use of molybdenum for metal substrate cells were examined, and cells were successfully made on silver and copper substrates, both of which would be cheaper than molybdenum. The plastic substrate cells were now front-wall devices, so that a continuous metallic coating, to provide a suitable surface for CdS deposition, had to be applied to the substrate. A vacuum metallization process with gold, as used by the RCA group in their original work with plastic substrates, was used at first. However, it was found to lead to too large a series resistance in 3" x 3" cells, and an alternative process was developed which allowed cells on plastic substrates to be made with efficiencies equal to those of metal-substrate cells. The plastic substrates were

¹⁶ With the exception of some work during 1967, in which CuBr was used on a trial basis for the barrier dip solution during operation of a pilot line for cell production (see below), further results in this area of investigation appear not to have been reported.

coated with a conductive polyimide varnish loaded with silver, which was cured and then coated with a thin layer of zinc. The varnish provided good adhesion to the substrate, and the CdS layer in turn adhered strongly to the zinc, simultaneously forming a low-resistance contact. Alternatives to the earlier use of gold grids were also examined, since these provided an appreciable part of the cell cost. Cells were made with high efficiencies using copper mesh, which became the standard material for grids during 1965.

Methods of grid attachment were also investigated; this was related to the broader question of cell stability. Testing showed variable behavior among the cells, some cells on metal substrates retaining their original efficiencies (around 5%) for periods of more than a year, under dry storage and vacuum thermal cycling. These cells were made with gold grids attached by nylon-Mylar lamination. However, under storage conditions allowing moisture absorption by the nylon, (which was found to be hygroscopic and to swell on absorbing water), severe cell degradation was observed. This degradation was ascribed to separation of the grids from the barrier layer, caused by swelling of the nylon. On relamination, degraded cells could be returned to their original efficiencies. Attachment of grids with conducting epoxy was expected to eliminate this problem. However, it was found that degradation of cells with epoxy-attached grids also occurred, which was found to be due to loss of adhesion between the silver-loaded epoxy and the copper grids, a condition which could be aggravated by temperature cycling. The provision of a silver electroplated layer on the copper grids was found to improve the adhesion, and it was decided that these would be used in the future.

The use of alternative encapsulant layers (thicker Mylar, and Kel-F) was found to apparently reduce the moisture penetration, without completely eliminating it.

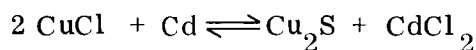
The question of coatings for CdS cells was also tackled by the group at Harshaw Laboratories under NASA funding (419). Most of the work was done on the deposition of glass layers by rf plasma sputtering. Although adherent layers were eventually obtained, it was found very difficult to apply sufficient power, as needed for adequate deposition rates, without heating the cells too much. The adhesion of evaporated films of SiO and MgF₂ of reasonable thickness (3-8 μ m) to the cell surface was found to be not adequate. Of the objectives, to obtain both better efficiency by providing antireflection coatings and I-R emitting surfaces to reduce cell temperature, and better stability by providing moisture barriers, some progress was made only toward achieving the I-R emissive surfaces. The difficulties encountered were sufficiently large to make further work appear to be not worthwhile.

During 1965, the USAF funding of the work at Harshaw terminated, but the NASA support continued (420). Cell efficiency increases as striking as those attained by the Clevite group had not been obtained, a performance of 3.52% conversion efficiency being the best seen during 1965. However, the electroplated grid process was improved until it provided a yield of operating cells of over 80%. In their work on

cell fabrication, the Harshaw group concentrated on the use of electroplated grids. The reason for this seems clear: the use of separate electroformed grids was proving to be a major obstacle to the achievement of stability for the Clevite cells, and the electroplated grids had been shown to give exceptional stability. Although electroplated grids yielded lower efficiency cells, it was felt that ways could be found to overcome this problem. Unfortunately, the solution to this problem was not as easily found as might have been hoped, so that the efficiencies of cells with electroplated grids remained lower than those of cells with mechanically attached mesh grids.

A principal aim of the most recent Harshaw work has been to establish a viable model for the cell as an aid to understanding its operation. During 1965, Hill and Keramidas determined that the cell contained a surface barrier region of non-stoichiometric degenerate p-type Cu_2S in contact with the n-type CdS (421), a structure which was similar to earlier suggestions. More importantly, however, they proposed that the region of CdS adjacent to the Cu_2S layer contained complementary concentration gradients of Cd^{++} and Cu^+ ions, and that solid-state diffusion of these ions accounted for changes in the cell properties, especially the spectral response, on heating the cell. It was also felt that these electrically active ions could be sufficiently mobile to cause appreciable changes in cell behavior even at room temperature. The implications of this ion motion for cell stability, as well as the evidence for and against its actual occurrence have been debated ever since.

The main evidence for the occurrence of ion motion in CdS cells at room temperature is a hysteresis effect, which was studied by both the Harshaw and Clevite groups, starting in 1964 onwards. This hysteresis is seen in the I-V characteristic of the cell, as shown in Figure 72. Such loops can be caused by junction capacitance and are then seen at audio or higher frequencies. However, this hysteresis is seen when curves are traced over long periods of time, so that explanation of this effect requires a search for processes with corresponding time constants. The Clevite group measured the hysteresis effect over periods of some minutes, and proposed that the mechanism for the effect involved thermal emptying of trapping levels, an effect which is frequently observed in photoconductor studies using CdS . The Harshaw group, however, observed the hysteresis effect over periods of 48 hours and more. This led to the interpretation in terms of ion diffusion by the Harshaw group in 1966 (420, 422), and, with some assumptions about the magnitude of ion motion needed to cause the observed electrical effects, diffusion constants could be calculated which were reasonably consistent with published data obtained by other methods. This ion movement was emphasized in a revised model, published in 1967 (423). The dependence of the spectral response on cell operating temperature was shown to be explicable in terms of shifts in the chemical equilibrium



This would imply that CuCl and CdCl_2 were present in the cell after fabrication. Measurements of junction capacitance as function of reverse bias voltage were performed to determine the distribution of the fixed charge in the junction region, using the effect analyzed by Shockley and mentioned in Section III-D-2-b. These measurements showed that the cell behaved as if it contained an abrupt p-n junction. The two interpretations:

- a. that the Cu^+ and Cd^{++} ions are mobile at room temperature, and
- b. that the p-n junction is abrupt,

are still disputed by other workers in the field, as is the postulate that the finished cell contains free Cu^+ , Cd^{++} , and Cl^- ions. The disagreement may result from real differences between cells which arise from differences in the fabrication procedures used by the various groups.

The latest advance in cell manufacturing methods took place during 1966. The Clevite group discovered that the improvement in cell stability, hoped-for through the use of silver-plated copper grids attached with silver-loaded epoxy, was not obtained (424). Under temperature cycling, a steady loss in cell efficiency was observed, resulting mainly from a reduction of cell voltage. This behavior was different from previous

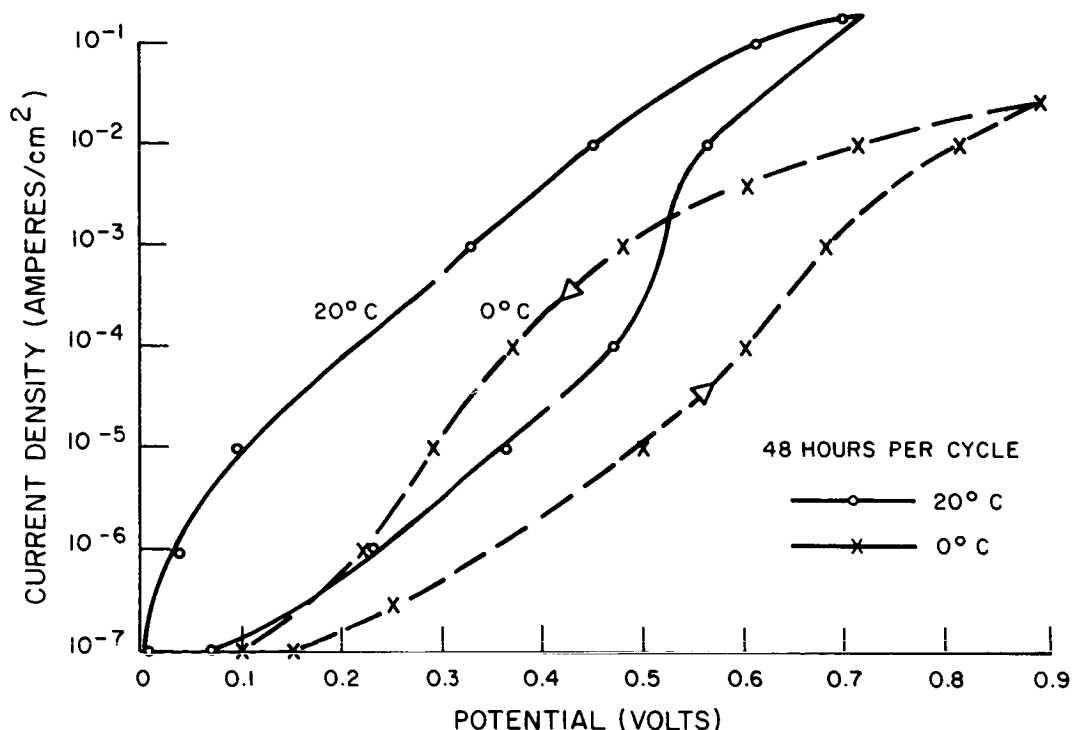


Figure 72. $\log(I)$ as a function of (V) for a CdS cell, showing the hysteresis effect (Harshaw data).

degradation effects, which had always been traceable either to short-circuits in the cell or to an increase in series resistance, both leading to loss of fill-factor and current. It was now postulated that stresses caused by differential thermal expansion between the grid and the CdS layer were causing a buildup of work damage in the CdS, resulting in loss of V_{oc} .¹⁷ The use of gold as a filler in the conducting epoxy, in place of silver, was found to eliminate the problem, when used in conjunction with gold-plated grids.

The hygroscopic nylon adhesive layer was also removed from the cell design, a clear epoxy being substituted. This was sprayed onto the Mylar or Kapton encapsulant film before lamination, and was cured by heating to 190°C during lamination, followed by a heat treatment at 80°C or above for a period of some hours to complete the curing. Humidity testing (80% RH) showed that this change definitely improved cell stability, and a good proportion of cells with gold grids and epoxy lamination were found to have degraded less than 5% under several thousand temperature cycles, and under 2 to 7 months of humid storage. In addition, high-temperature (100°C) vacuum storage tests were run. These tests gave variable results, from severe degradation (no output after 16 weeks), to complete stability (no apparent change after 16 weeks).

Although these test results indicated that the stability problem with the cells was not solved, the Clevite group took them as evidence against the possibility of degradation by ion diffusion, as implied by the Hill-Keramidas cell model, since some cells showed complete stability through these tests.

Improvements in the cell power-to-weight ratio were also made during 1966 by the Clevite group. Use of the metal substrate was temporarily discontinued, and the plastic substrate and encapsulating films were reduced in thickness from 2 to 1 mil. In addition, the grid mesh was improved from 60 x 60 lines-per-inch to 60 x 10 lines-per-inch, the nominal line width remaining 1 mil. This improved the optical transmission from 85 to 91%.

The typical performance of the better Clevite 3" x 3" (55 cm²) cells at this time was:

Efficiency:	6.0%
V_{oc} :	0.50 volts

¹⁷ One is tempted to speculate on the possibility of the silver playing an active part in changing the crystallographic structure of the CdS in contact with the epoxy, because of the striking effects seen by Van Cakenberghe and others on the recrystallization of CdS by the use of silver, even though the temperatures used in the Van Cakenberghe process are higher than those achieved in the temperature cycling.

I_{sc} :	0.960 A (17.5 mA cm ⁻²)
F:	0.67
R_s :	0.06 Ohm

all measured under 100 mW. cm⁻² sunlight equivalent. At this time began an appreciable effort to produce larger quantities of cells, coupled with a tightening of process control, and the establishment of standard processing methods to increase production yield and device uniformity. This was apparently the reason why the very high efficiencies obtained occasionally during earlier work have not been seen since, although the average cell efficiencies have been maintained near 5%. It seems that the processes for which control and reproducibility have been obtained, are not identical to those which previously led to the highest cell efficiencies. Some processes may also be inherently difficult to control, and it is perhaps for this reason that the replacement of HCl with HBr or HI in the barrier formation process has not been pursued further.

Additional work has been done at Clevite on production methods for thin-film CdS cells under NASA funding in the period 1966-present, but reports on this are not yet available (425). The latest report on the status of Clevite cell fabrication appears to be that given by Hietanen and Shirland in 1967 (426). Substrates in use are both copper foil and silver-varnish coated polyimide plastic, both given a thin coat of zinc before CdS deposition. The CdS is 20 μ m thick, the barrier is formed by etching the CdS in HCl, dipping in CuCl for about 5 seconds at 90°C, rinsing and then heating in air to about 250°C for 2 minutes. Gold-plated copper grids are attached with gold-loaded epoxy, and Mylar or Kapton sheet encapsulant is attached with transparent epoxy.

Substrate and grid extensions serve as contact tabs, the total cell thickness is 3.2-3.5 mils, and the active area is 55 cm². Efficiencies are near 5% average under 100 mW. cm⁻² sunlight. Stability, although much improved, continues to show variable results, some cells being completely stable under storage and vacuum thermal-cycling tests, other cells showing degradation.

Reference 426 also reported a suggestion by Spakowski that a compromise between the high optical transmission of the Mylar encapsulant and the good UV resistance of the Kapton encapsulant could be achieved by applying an 0.2 mil thick layer of Kapton as a polyimide varnish on Mylar-encapsulated cells. The Kapton presumably would absorb the UV sufficiently strongly to protect the underlying Mylar, while not being sufficiently thick to give appreciable optical absorption in the main range of spectral sensitivity of the cell.

In addition, a second series of projects has recently been funded at Clevite by the USAF. During 1966-1967, a pilot line was operated to optimize manufacturing methods and to make cells for balloon and space flight testing (427). Some of the manufacturing process variations were:

- a. Copper doping the surface region of the CdS layer either by introducing copper during the deposition of the top 2000-5000Å of the semiconductor layer, or by evaporating a 200-1000Å thick layer of Cu onto the CdS layer.
- b. Introducing chlorine into the CdS layer.
- c. Evaporating a layer of Cu₂S onto the CdS surface prior to the CuCl dip process.
- d. Heat treating the CdS layer under various ambients prior to barrier formation.
- e. Dipping the films in Na₂S or CdCl₂ solutions prior to barrier formation.
- f. Making the barriers by dipping in CuBr rather than CuCl.
- g. Forming the Cu₂S layers by vacuum deposition of Cu₂S, followed by immersion in Na₂S to produce the non-stoichiometric Cu_{1.8}S believed to be formed by the dipping process.
- h. Forming the Cu₂S layers by vacuum deposition of Cu followed by immersion in a solution of sulfur in benzene.
- i. Using a solution of CuCl in acetone for the barrier-formation dip process.
- j. Heat-treating the cells under various ambients after barrier formation.

In no case were more efficient or stable cells made than those produced by the standard processes.

Of the cells made for flight testing, the first group delivered was of the type in which the grids were attached by the nylon-Mylar lamination method. As would be expected from the results described above, these failed by delamination during preflight testing.

Other cells delivered used grids attached by gold-epoxy, and had Kapton lamination attached by clear epoxy to provide UV resistance (though at a sacrifice of performance: the arrays delivered only 3-4% conversion efficiency). Results on flight testing of these cells have not yet been reported.

Starting in June 1966, the USAF has funded a continuing series of studies at Clevite by Shiozawa and others, aimed at providing an understanding of the known experimental facts of the CdS thin-film cell (428). During the first year, a cell model was developed which provides a good fit to the experimental facts. This is termed "model 1066",¹⁸ and postulates that the barrier region of the cell contains three layers, as shown in Figure 73. The intrinsic CdS layer arises from the presence of allowed electron energy levels near the center of the forbidden band gap, as shown in Figure 73a. These levels are caused by the presence of copper atoms, and act as traps for the conduction electrons, which were contributed from the donor levels near the conduction band. The Cu₂S is highly degenerate p-type (10^{20} holes cm⁻³), and the collector grid makes an ohmic contact to this layer. The substrate forms an ohmic contact to the CdS, and the junction between the intrinsic and the n-type CdS provides the region of main photovoltaic activity. A revised model ("1067") has since been presented, in which it is proposed that the band structure is as shown in Figure 73b, and the photo-active barrier is the Cu₂S-(i)CdS junction.

In the dark, the device should behave as a rectifier, but with a rather high series resistance arising from the intrinsic CdS layer. Under illumination of the Cu₂S surface, it is assumed that most photons with energies not greatly exceeding the band gap of Cu₂S (1.2 eV) are absorbed in the Cu₂S, but that a portion of the photons with energy above 2.5 eV penetrate into the intrinsic CdS region, create electron-hole pairs there and fill up the electron traps. The photo-produced excess holes in the Cu₂S diffuse to the collector electrode, and the electrons diffuse into the intrinsic CdS region, where they are accelerated by the electric field, and enter the n-type CdS. This model therefore explains the major features of the CdS cell:

- a. The spectral response is governed by the energy gap of the Cu₂S (1.2 eV) rather than by that of the CdS (2.4 eV), thus accounting for the extrinsic spectral response.
- b. The photoconductivity of the intrinsic CdS region accounts for the experimentally observed crossing of the light and dark I-V characteristics. (This effect is shown in Figure 74).
- c. The spectral response of the photoconductivity of the intrinsic CdS should increase in the green spectral region (near the 2.4 eV band edge), and hence green bias light will lower the series resistance, which accounts for the enhancement of the red response when green light (or white light) bias is applied.

¹⁸ It was proposed during October, 1966.

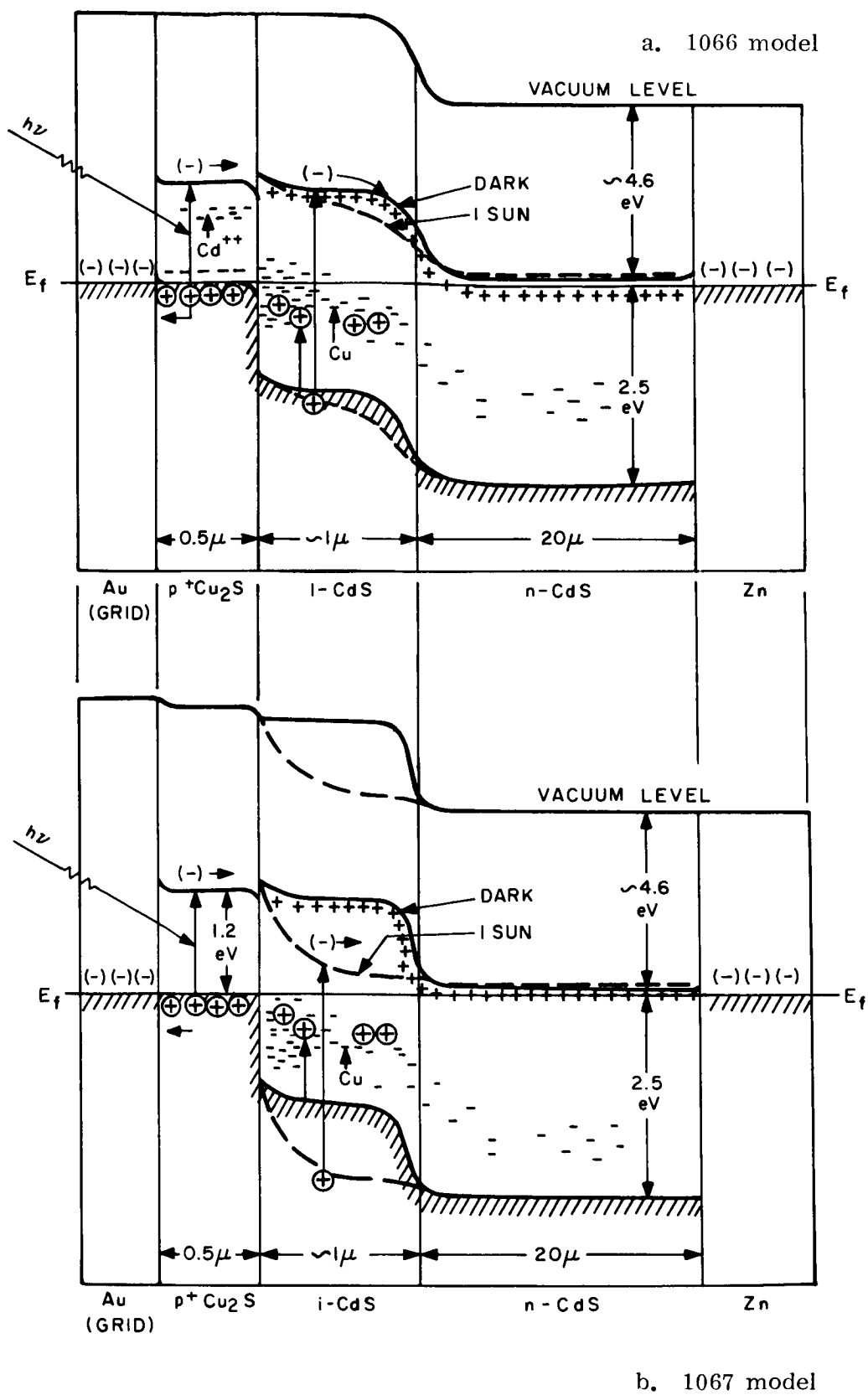


Figure 73. Clevite group's proposed band structures for CdS cells.

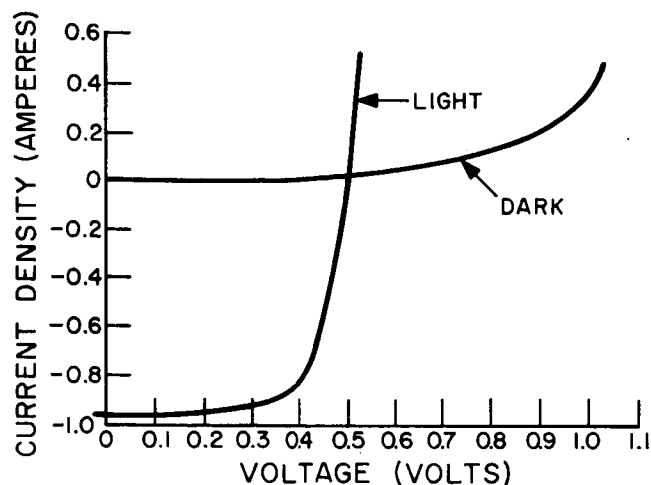


Figure 74. I-V curves for a CdS cell in the light and the dark, showing crossing of the two curves.

- d. The V_{oc} of the cells should be governed by the material with the smallest energy gap, i. e., the Cu_2S , and the V_{oc} values seen in practice are consistent with this ($E_g = 1.2$ eV, $V_{oc} = 0.4-0.5$ V).

A large number of experiments to support this model were reported, for the details of which the reader is referred to the original reports. The measurements included data on the Cu_2S layer thickness and stoichiometry, the optical properties of Cu_2S (including evidence for a second conduction band minimum at 1.85 eV), diffusion and solubility of Cu in CdS, capacitance and I-V curve measurements on the cells, and spectral response measurements. These supported the "1066" cell model, the difference between the "1066" and "1067" models being only in the detail of the change in band structure in the i-CdS layer under illumination. The effect of this change is that the photoactive region occurs at the Cu_2S -iCdS junction, as shown in the diagram. This change was made after experiments which allowed the estimation of the carrier densities in the i-CdS region. This showed that the electron quasi-fermi level in the intrinsic CdS region must move close to the conduction band edge under illumination at the intensity used in cell operation.

A chemical analysis of the Cu_2S formed by immersion of CdS in CuCl solution was also performed during this work, and the result was at variance with the results obtained during earlier analysis of this material. The previous results had indicated that the Cu_2S layer on the cells was non-stoichiometric, with a composition close to $Cu_{1.8}S$, the same as that of the stable mineral digenite. Shiozawa's group obtained data indicating a stoichiometry of $Cu_{2.0025}S$. Although a small proportion of the copper could be accounted for by incomplete rinsing of the CuCl solution from the crystals, and the presence of Cd^{++} in the Cu_2S , this result indicated that the stoichiometry of the chalcocite form of Cu_2S (whose presence in the cells was inferred from X-ray diffraction data) must be close to the nominal value of Cu_2S .

Work on cell fabrication is continuing under Shirland at Clevite, recently under USAF sponsorship (429). At the moment, attention is being focused on evaluating various conducting adhesives for attaching the grid to the Cu_2S surface of the cell, in an attempt to improve cell efficiency and obtain cell stability. Best results have been obtained with gold-filled epoxies, confirming the earlier results.

The most recent Harshaw work was funded by NASA, and was a direct follow-on to the previous research. The Harshaw group has now terminated work in this field, and their final report on this contract therefore summarizes their achievements (430). During this latest period, work was aimed at improving conversion efficiency, cell stability, and manufacturing process control.

Close-spaced vapor transport was investigated as an alternative to vacuum evaporation for making the CdS layers, but lower efficiency cells were obtained than from the normal vacuum-deposition process. The growth habit in the films formed by vapor deposition tended to produce whiskers, indicating that these layers had a surface which was different from that of the vacuum-deposited layers. Hence the dip process (whose results can be assumed to depend to some degree on the details of the surface condition of the CdS) may not have been well-suited to the vapor-deposited CdS.

The doping of CdS films, to improve cell efficiency by controlling the carrier concentration, was also investigated. After overcoming various technical problems, some control of CdS layer doping and carrier concentration was achieved, but again low cell efficiencies were obtained. This was partly due to low V_{OC} values, and partly due to high series resistance probably arising from poor contact between CdS and molybdenum substrate caused by the changes in CdS layer growth conditions, these changes being necessary to obtain control of carrier concentration.

Alternatives to the dip process were examined with the objective of eliminating water from the cell processing steps, since moisture is known to play a part in cell degradation. The use of molten salt baths consisting of eutectic mixtures of cuprous salts with other salts to give reasonably low molten temperatures (120-300°C) gave working cells. However, the high temperatures led to reactions so rapid that short dip times were necessary and could not be accurately controlled. The use of cuprous ion dip solutions using organic solvents was also evaluated. Best results were obtained with a mixture of lithium and cuprous iodides in ethylene glycol. By adjustment of the process parameters (dip time and temperature, and post-dip heating time and temperature), good cells were made by this method, with efficiencies typically around 3-4% and having a best value of 5.4%. Results indicated that good V_{OC} values (up to 0.55V) could be reproducibly obtained, but that J_{SC} values were low, typically 10-14 $\text{mA}\cdot\text{cm}^{-2}$, with a peak of 16 $\text{mA}\cdot\text{cm}^{-2}$. Available effort did not allow exhaustive evaluation of this approach, and the Harshaw group felt that with further work it could prove a serious alternative to the aqueous dip process. Interestingly, a dip bath of sodium and cuprous

bromides in ethylene glycol was found to give good but inconsistent results, which is reminiscent of the effects seen by Clevite in examining CuBr aqueous dip processing.

In investigating the efficiency increases which could be obtained by changing the grid application method, grids were applied by various electroplating processes, and by attachment of electroformed grids. With the electroplated grids, it was found that plating times had to be minimized to prevent water from the bath degrading the cell. It was also found necessary to use a first-covering layer free from copper at the start of grid deposition, since copper directly in contact with the barrier layer was found to convert the barrier material to cupric sulfide, leading to low V_{oc} values. Using cyanide-free plating solutions, permitting rapid deposition of grids to minimize plating time, cells were made with efficiencies up to 5.3% for a 44 cm² cell. The use of electroplated grids was discontinued part way through the contract, and it was felt that the higher-quality CdS layers available later would have permitted higher efficiencies to be achieved with the electroplated grids.

Cell encapsulation was achieved using Mylar attached with nylon, which was changed later to Mylar attached with epoxy. Increased stability was achieved in the latter case, as shown by the Clevite work. After encapsulation, the substrates were thinned from 2 mils to 0.3-0.5 mils by etching.

In operation of a pilot line, cells were made by vacuum deposition of CdS onto sand-blasted Mo substrates. Following etching of the CdS layer with H₂SO₄ or HCl, the barrier was formed by aqueous cuprous ion dip followed by a heat treatment, and a gold-plated electroformed copper mesh was then applied to the CdS surface by passing the cell/grid combination between heated rollers. The Mylar or Kapton encapsulant was finally applied, by lamination with nylon or epoxy adhesive. 800 (3" x 3") cells were made, with average efficiencies around 4%, and a maximum efficiency of 4.5%. Experimental cells made by this process gave a maximum efficiency of 7.1% for a 3.4 cm² device. This then is the present state of the research at Harshaw and Clevite. The Harshaw group has recently stopped working in this area, and the Clevite group is making cells on a modest commercial scale, while continuing research on cell fabrication and degradation (under NASA and USAF sponsorship) and mechanism of operation (under USAF sponsorship).

Although most of the important practical aspects of the CdS thin-film cell have been established by work in commercial laboratories in the U. S. A. (at Clevite, Harshaw, NCR, and RCA), other workers have also made contributions to this field. The first of these was of course D. C. Reynolds, whose pioneering work on single-crystal cells, followed by the support he has provided through the contracts of the USAF with commercial laboratories for research on thin-film cells, make him foremost in this field. Dr. A. Potter of the NASA Lewis Research Center, in many respects the counterpart of Reynolds at Wright-Patterson AFB, has also not only provided technical support for the research contracts between NASA and industry, but has in addition made major contributions to the field.

In 1967, Potter advanced a cell model with the following major features (431, 432):

- A p-type barrier layer of highly degenerate chalcocite (orthorhombic cuprous sulfide).
- A band structure as shown in Figure 75, giving a barrier height of 0.85 eV.
- Photoemission of electrons from the Cu_2S valance band into the CdS conduction band over the 0.85 eV barrier giving the extrinsic red response.
- Photoemission plus intrinsic CdS response accounting for the blue sensitivity.
- The efficiency of photoemission being controlled by impurities in the CdS layer in the junction region, with the occupancy of these impurity levels variable by blue illumination, thus accounting for the effect of high-energy bias light on the red response.

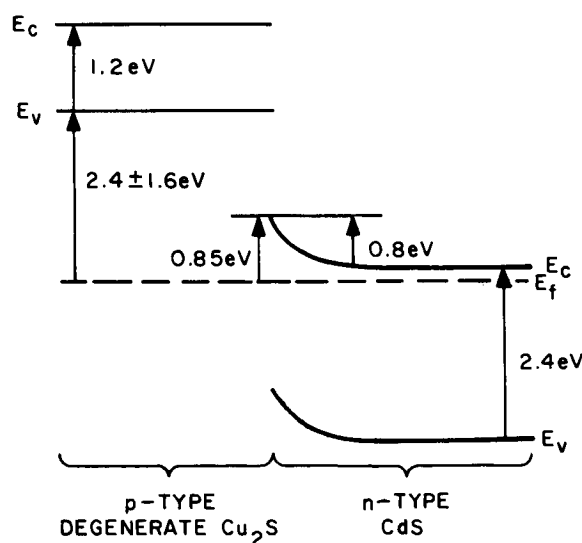


Figure 75. Band structure for active junction of CdS cell, as proposed by Potter.

More recently, however, Potter has provided evidence and support for the "1067" cell model of Shiozawa (433). This evidence included data on spectral response measurements, showing particularly the effect of green bias light on red response. It was also shown that R_g for the cells is reduced by a factor of 100 by green illumination, and that this also affects the value of the empirical constant A in the diode equation, as analyzed by Shiozawa. Potter also pointed out that the photoconductivity of CdS is much impaired by water, and this may be the origin of the degradation of CdS cells by moisture. It appears that the dialogue between Potter and Shiozawa may succeed in unravelling the mysteries of the CdS cell, and hence provide a major step forward in this research field.

Since 1963 an independent testing program for CdS cells from industry production has also been in operation under Spakowski, at the NASA Lewis Research Center and the results were reported in 1966 (434, 435). Thermal cycling under vacuum was performed with automated equipment simulating earth orbit conditions, with cell temperatures oscillating between -100°C and room temperature, and illumination by a xenon arc sunlight simulator. The results showed that metal-substrate cells with electroformed grids attached by lamination with nylon failed within a few hundred cycles, by developing short circuits. Cells on metal substrates with grids attached by conducting epoxy failed by loss of adhesion between epoxy and grid (these were presumably cells made by Clevite using silver-loaded epoxy, though this is not stated in the Technical Note, reference (434)). Cells on metal substrates with electroplated grids successfully withstood 3400 thermal cycles, but the starting efficiencies were low (these were presumably Harshaw cells, though again this was not stated). Cells on plastic substrates with grids attached by nylon/Mylar encapsulation were found to be stable (one cell successfully withstood 16,000 cycles between -85 to 61°C), but most of the cells used were low-efficiency units, and the better efficiency cells were only cycled 2,200 times before termination of the test.

In moisture degradation experiments, cells with nylon adhesive showed extensive degradation by increase of series resistance when exposed to humid environments, the rate of degradation being proportional to the humidity. Cells which had degraded to an output of 50% or more of the initial value could be restored by heating (presumably to dry out the cells), but cells which had degraded to give less than 50% of their initial output suffered irreversible changes. Cells encapsulated with Kapton polyimide degraded more rapidly than those with Mylar, because of more rapid permeation of water through the former. However, tests run on later cell types with the encapsulant attached with transparent epoxy successfully withstood storage for periods of up to 109 days under 66% relative humidity, indicating that this moisture degradation problem has been largely solved.

Work has also been proceeding under Hui of RCA Astro-Electronics Division, at RCA Laboratories. This has been supported mostly by internal funding during the period 1962-present, with primary emphasis being placed on the development of processes which would enable cells to be made with in the form of integrated, series connected arrays, formed as such during the cell fabrication. This would reduce the cost of space power systems by eliminating most of the interconnections needed to build up present type arrays.

The first results were obtained with backwall cells made on tin oxide coated glass substrates, with two cells series connected (402). These exhibited low efficiencies (1%), so that subsequent work during the period 1962-1964 was aimed primarily at improving single-cell conversion efficiencies. The sought-for improvements were obtained, the cell structure was changed to the front wall type, and in 1965 attention was turned once again to array fabrication. Initial results were obtained with arrays of cells made on plastic substrates, using electroformed grids attached during encapsulation (436). Early efficiencies obtained were 5.1% under $86\text{ mW}\cdot\text{cm}^{-2}$ sunlight in a 2-cell array of 10.8 cm^2 total area, and 4.72% in a 4-cell array. Subsequent work was directed towards improved efficiency, achieving better process control,

and developing processes suited for mechanized production, like all-vacuum processing of the arrays. As part of the latter goal, recent work has been concerned with the replacement of the electro-formed gold grid with an evaporated-grid structure. Progress has been made to the point where vacuum-deposited gold grids have been successfully applied to make 4-cell arrays of 16 cm^2 total area. Recent efficiencies have been up to 5.3% under 86 mW.cm^{-2} sunlight on 16 cm^2 , 4 cell arrays, with average values near 5%, and 70% yield for arrays above 4%. Best single cell efficiency in these arrays was 6.6%. These efficiencies were similar to those achieved on the pilot line of the Clevite group, but the work on array concepts is believed to be unique. The implications of this rather different approach to CdS cells will be further discussed in the next chapter.

Remarkably little work on thin-film CdS cells appears to have been done in countries other than the USA. In 1966, Balkanski and Chone (of French government research laboratories) discussed their results on photoconductivity and the photovoltaic effect in thin-film CdS devices (438). The CdS layers of $20 \mu\text{m}$ thickness were deposited on aluminum electrodes on glass, on aluminum foil, and on plastic (Kapton polyimide) metallized with gold or aluminum, by evaporation under vacuum. The barriers were formed by vacuum deposition of a thin (semitransparent) layer of copper, followed by vacuum deposition of a copper or gold grid pattern and by a heating cycle to 300°C . An aqueous chloride ion solution was then applied, followed by a second heating cycle. The resulting cells showed overall conversion efficiencies of 1.1%, or net efficiencies of 1.45% (subtracting the area of the cell covered by grid lines; actual cell areas were not reported). The I-V curves showed clear evidence of R_s degrading the cell performance.

In 1967, Bujatti of the Institute of Physical Optics in Zagreb, Yugoslavia, reported work on an investigation of the barrier height at a metal-insulating CdS junction (439). Although the work did not involve CdS solar cells, the use of evaporated CdS layers with photovoltaic metal contacts indicates the potential to develop such cells in an East European country.

In 1967, Te Velde of Philips Laboratories, Eindhoven, reported results obtained with thin-film CdS cells made by wholly different techniques (440). The basic concept underlying these cells had been described earlier by others (see the sections on silicon cells made of spheres, IV-B-3-a, and on GaAs thin-film cells, IV-D-4). This involved embedding grains of CdS in a plastic binder, to form a layer of CdS on a plastic film. The grains were treated to form a surface barrier before embedding, and the immersion in the plastic was only partial, so that the exposed surface of the CdS could be etched to allow contact to be made to the bulk of each grain. Efficiencies exceeding 0.5% were not obtained, and further work using this approach is apparently not planned.

This completes the account of the work on CdS thin film cells up to the present time. The field has been one of the most fruitful areas of cell research, and the successes which have been achieved indicate that commercial production and utilization of these cells may not be far away. However, some problems have not been wholly solved, and an evaluation of the work which has been done in the past, and its implications for the future, will be presented in Chapter V.

3. Cadmium Telluride

Theoretical calculations showing the dependence of conversion efficiency on semiconductor bandgap, such as that of Loferski (185), indicated that cadmium telluride should be a suitable material for solar cell fabrication. This prompted work on single-crystal CdTe cells, as described in section IV-C-5 above, starting in 1955.

In 1960, the General Electric Research Laboratories studied a number of possible ways of making unconventional solar cells, under contract with the USAF (441). One of the main areas of investigation during this work was an examination of the feasibility of making polycrystalline thin films of CdTe suitable for solar cells. Methods were developed for making low-resistivity thin films of both n- and p-type CdTe, and the electrical and optical properties of these layers were measured.

It was found that although CdTe layers could be obtained by conventional vacuum evaporation of the compound, suitable crystallinity in the deposited layers could be obtained only if the substrate temperature was maintained at about 600° C. When a conventional bell-jar evaporator was used, re-evaporation of CdTe from the substrate onto the cold walls of the vacuum system prevented suitable films from being obtained. It was found, however, that if a vacuum enclosure with heated walls was used, this problem was circumvented, and deposition rates of 20 $\mu\text{m}.\text{min}^{-1}$ could be obtained with a CdTe source temperature of 1600° K. Conductivity type for the deposited layer was controlled by co-evaporation of either In (for n-type) or Cu (for p-type).

An alternative to the vacuum evaporation of the compound was also investigated during this exploratory work, and was developed further during subsequent contracts. CdTe was deposited by co-evaporation of cadmium and tellurium, the vapors reacting on the heated substrate to form CdTe. This process also used an evacuated reaction chamber.

Substrates used included quartz, various glasses, mica, sapphire, molybdenum and tantalum. Of the insulating materials, sapphire proved the best (good adhesion between substrate and CdTe being the criterion). Both molybdenum and tantalum were found to be also satisfactory.

Crystallographic studies and luminescence emission spectra studies were made on single-crystal CdTe. An important point also established during these studies was that the optical absorption constant in CdTe rises sharply beyond the absorption edge, indicating a direct optical transition process (see Figure 66). Thus adequate optical absorption for high conversion efficiency should be obtained in a thin layer of CdTe, as discussed in the introductory paragraph of this section (IV-D-1 above).

Contacting methods were developed for the CdTe films, using evaporated Au, Ag, or Cu for p-type material, and, for n-type material evaporated In followed by a 350° C heat treatment.

The fabrication of p-n junctions was attempted by sequential deposition of n- and p-type films, but it was found that high-resistivity layers were obtained, presumably because at the 600° C substrate temperature diffusion of dopants between adjacent layers occurred to a sufficient degree to cause compensation. The diffusion of copper into an n-type film from a vacuum-deposited copper film, to form a p-type region adjacent to the CdTe surface, resulted in an indication of rectifying action, though the junction was not of good quality.

In the space of less than a year, then, the feasibility of thin-film CdTe cells was demonstrated. The most significant point established during this early work was the experimental ability to make films of both n- and p-type conductivity at will, with reasonable conductivities. This is most unusual, the normal case being that even if a semiconductor can be made with controlled conductivity type in single-crystal form, thin films of the same material show a strong preference for one conductivity type, and the impurity concentration which must be introduced to over-compensate this preference is enough to appreciably degrade the semiconductor properties.

This encouraging initial work was immediately followed up by a program of research funded by the USAF. This program is still continuing, and the time spans of the various contracts are indicated in diagrammatic form in Table XX. During 1961 and early 1962, sufficient progress was made to allow operating solar cells to be made on single-crystal and polycrystalline CdTe cells (442).

The thin-film cells were made on both glass and metal substrates at this time. The glass substrates were coated with CdS to provide contact to the CdTe layer, but the metal substrates used (including molybdenum, zirconium, and titanium) formed an ohmic contact directly to the CdTe. The CdTe layers were about 10 μ m thick, and were deposited by reactive deposition of cadmium and tellurium vapors in the equipment shown diagrammatically in Figure 76. A mixture of dried cadmium and cadmium iodide was fed into the hot zone of the furnace down one feed tube, and tellurium powder was fed through the other tube. These components vaporized, the vapors reacting to form CdTe doped with iodine, which was deposited on the substrate and neighboring regions of the reaction vessel. A rough vacuum, (about 10 μ m) was held in the reaction chamber during deposition, which took about 30 minutes. The iodine doping produced n-type conductivity, with most films having a resistivity of about 10-1000 Ohm-cm., though it was found that lower resistivities could be obtained if additional gallium dopant was added, or if the films were quenched rapidly at the end of deposition.

It was found to be very advantageous (on the criterion of cell efficiency) to form a surface region with a lower n-type doping or even a light p-type doping by changing the film growth conditions towards the end of the growth period. This was done either by adding a p-type dopant such as copper chloride or arsenic to the powder mix introduced at the end of the run, eliminating the n-type dopant, or increasing the proportion of tellurium.

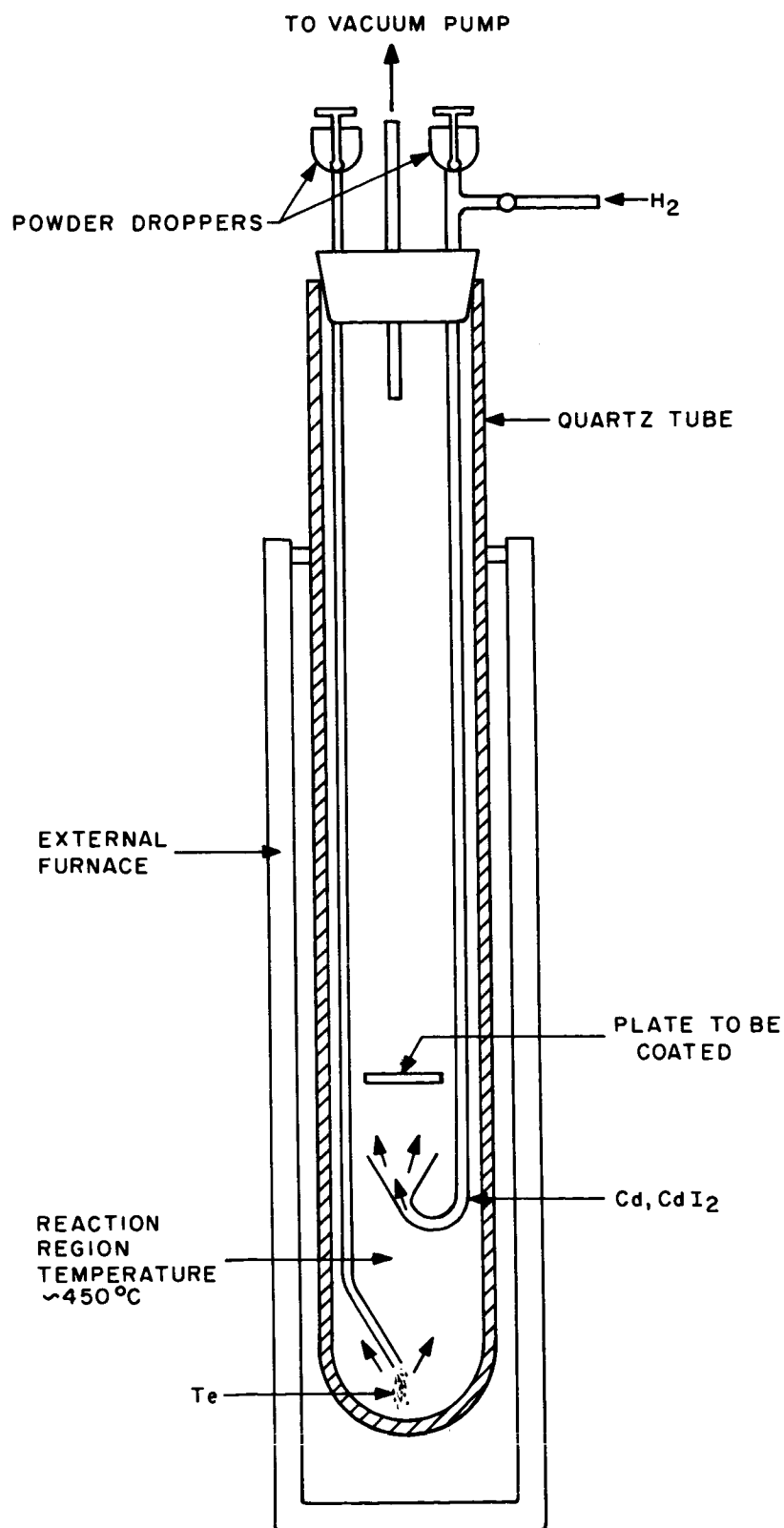


Figure 76. Cross-section of equipment used for reactive vapor deposition of CdTe layers, after Cusano.

The active barrier was then formed by dipping the CdTe film into a warm aqueous cuprous ion solution for a few seconds. This was found to form a thin surface layer of Cu_2Te , which was identified by electron diffraction measurements. The Cu_2Te barrier layer thickness was p-type, about 50-100 Å thick in the better cells, with a sheet resistance in the 100 ohms per square region, and a mobility of about $1 \text{ cm}^2\text{V}^{-1} \text{ sec}^{-1}$.

Contact to the barrier layer was made using electroformed gold or nickel meshes attached with pressure sensitive cellophane tape. Attempts to deposit grids by vacuum evaporation or by electroplating led to cells with lower efficiencies. The completed cell structure was as shown in Figure 77. Single-crystal cells were made using similar barrier-formation processes.

Spectral response studies of the completed cells showed that the devices exhibited only the expected intrinsic response characteristic of the CdTe bandgap, with a sharp rise in I_{sc} at 8250 Å, as shown in Figure 78.

I-V curve measurements under illumination indicated that conversion efficiencies of up to 6% under 87 mW cm^{-2} sunlight could be obtained with cells of small area (less than 1 cm^2). However, the efficiencies quoted were on an active or net area basis, i.e., they did not account for the cell area covered by grid lines. V_{oc} values were around 0.5V for film cells, with I_{sc} densities of up to 17 mA cm^{-2} and F values of 0.45-0.60. Electrical measurements were made over a range of temperatures and illumination intensities, the results being generally as would be expected, but with V_{oc} values going to 1.0 V for single-crystal cells at low temperature indicating the existence of a barrier height of at least 1.0 eV.

The cell was taken to be a heterojunction device, between n-type CdTe and p-type Cu_2Te . However, the Cu_2Te was believed to be degenerate, so that the depletion region existed almost wholly in the CdTe, while the Cu_2Te behaved essentially as a metal. The junction could therefore be alternatively viewed as a metal-semiconductor contact, with an inversion layer in the CdTe providing the barrier region field, and the Cu_2Te giving an ohmic contact to the p-CdTe surface layer. The proposed band structure was as shown in Figure 79.

A cell degradation problem also made itself manifest at this time, a 10-20% loss in efficiency being seen over a period of some two or three months even in the most stable cells. There was some indication that degradation was enhanced by the presence of water vapor, but otherwise little was known about the effect.

Progress was maintained during the period 1962-1964, under USAF funding (443-445, 413). Cells made during the later part of this period were all on molybdenum substrates, and few changes were made in the structure during this period. The resistance between the substrate and the CdTe was reduced by coating the molybdenum with a thin layer of CdS at the start of the CdTe deposition process. Alternatives were

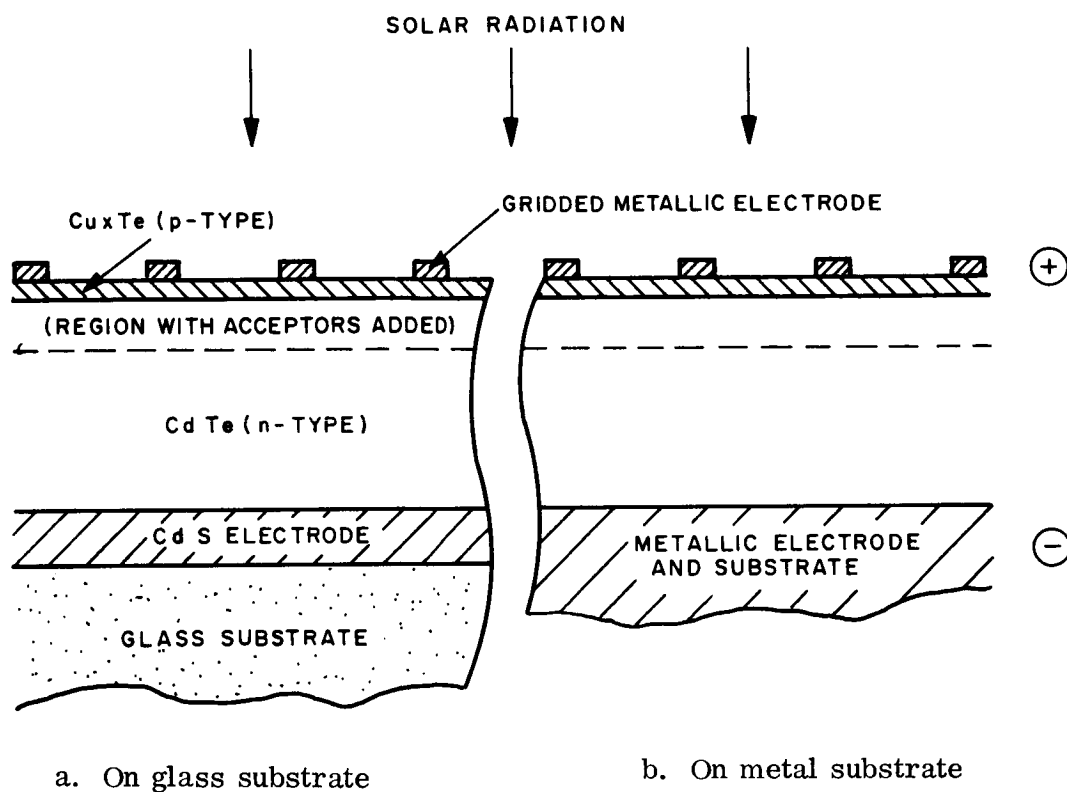


Figure 77. Cross-sections showing structure of CdTe cells.

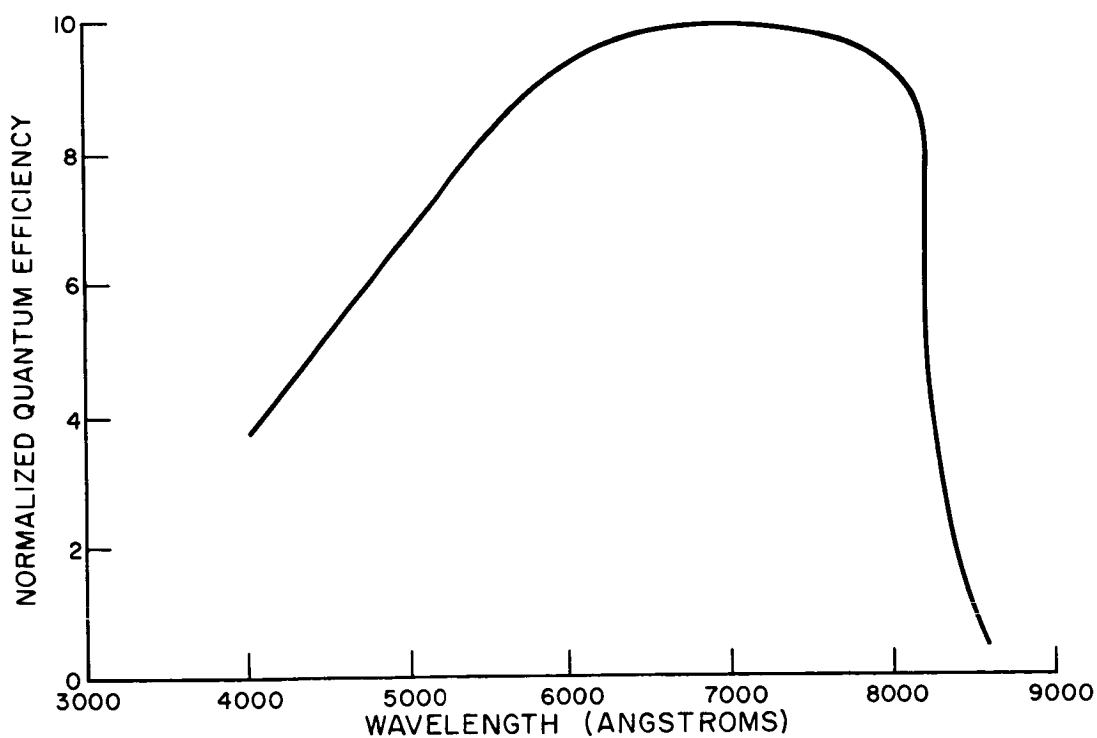


Figure 78. Spectral response curve for CdTe thin-film cells

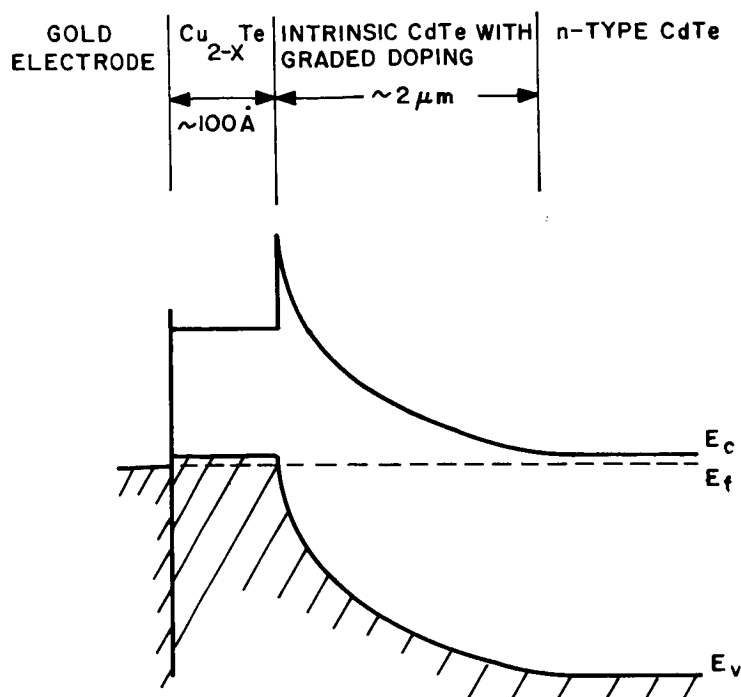


Figure 79. Band-structure proposed by Cusano for active region of CdTe thin-film cell.

sought for the collector grid, to replace the pressed metal mesh attached with cellophane tape. Vacuum deposited gold was found satisfactory for this. A "comb" structure of gold with a film thickness of $1-2 \mu\text{m}$, and a busbar of molybdenum ribbon running along the center of the cell, were used. This enabled cells to be made about 1 inch wide without the gold grid line resistance noticeably degrading the cell performance.

A major effort was made to improve film uniformity (both in thickness and electrical quality) by modifying the vapor reaction furnace used for the CdTe deposition. The principle of the method, and the materials and procedures used, remained substantially as already described, however. The equipment modifications allowed uniform films to be made on molybdenum substrates with areas up to 56 cm^2 , giving cells with gridded areas of 52.5 cm^2 .

The barrier formation methods remained as described above, with a graded resistivity region formed by programmed doping of the last portion of CdTe film growth, followed by dip treatment in CuCl_2 solution. The control over the graded conductivity region was improved so that the width of this region (and hence that of the junction depletion region) could be varied. It was found that the spectral response of the cells could be changed by altering the depletion region width, cells with a narrow depletion region

responding less to red light (which would be absorbed further away from the active junction) than cells with a wider depletion region. This showed that the high collection efficiencies measured in the more efficient cells probably arose because almost all optical absorption took place in the depletion (high-field) region of the cells. However, it was also found that if an attempt was made to make this depletion region too wide, then a reduced collection efficiency was obtained. This was thought to be due to the formation of a relatively field-free, uniformly doped, p-type conductivity region at the cell surface, the minority carrier diffusion length in this region being small, so that collection of minority carriers generated in this region would not be efficient.

With the process control improvements made during this phase of the project, device quality improved so that by the end of 1964 a cell was made with the following performance:

Area:	(Total) 56 cm^2 (Gridded) 52.5 cm^2	
Weight:	1.44 gms (including leads)	
I_{sc} :	774 mA ($14.7 \text{ mA} \cdot \text{cm}^{-2}$)	} under $85 \text{ mW} \cdot \text{cm}^{-2}$ sunlight
V_{oc} :	0.511 V	
Efficiency:	4.88% (gridded area) 4.58% (total area)	

The standard cell design at this time was a cell with overall dimensions 2" x 4", and with two collector grids and contacts applied as shown in Figure 80.

Various encapsulant materials were tried, with the objectives of providing mechanical protection, reducing optical reflection, and preventing moisture degradation. Two classes of materials were used; inorganic insulators (especially SiO_2), and organic polymers. Silica deposited by rf plasma sputtering was found to give the best moisture protection (as determined from stability measurements), but its deposition was found to degrade the cell performance by a factor of 2 to 3. Although about a half of this loss could be recovered by simply storing the cells, the final efficiencies seen were generally only around 3%. Of the organics, "Krylon"¹⁹ was found to give the best moisture protection, and cell performance was improved through a 10-12% gain in I_{sc} resulting from reduction of optical reflection as the result of its application. This was considered the best available coating material, but it was recognized that it was not

¹⁹ "Krylon" is a solution of a mixture of polymers of acrylic and methacrylic acids, and of acrylonitrile.

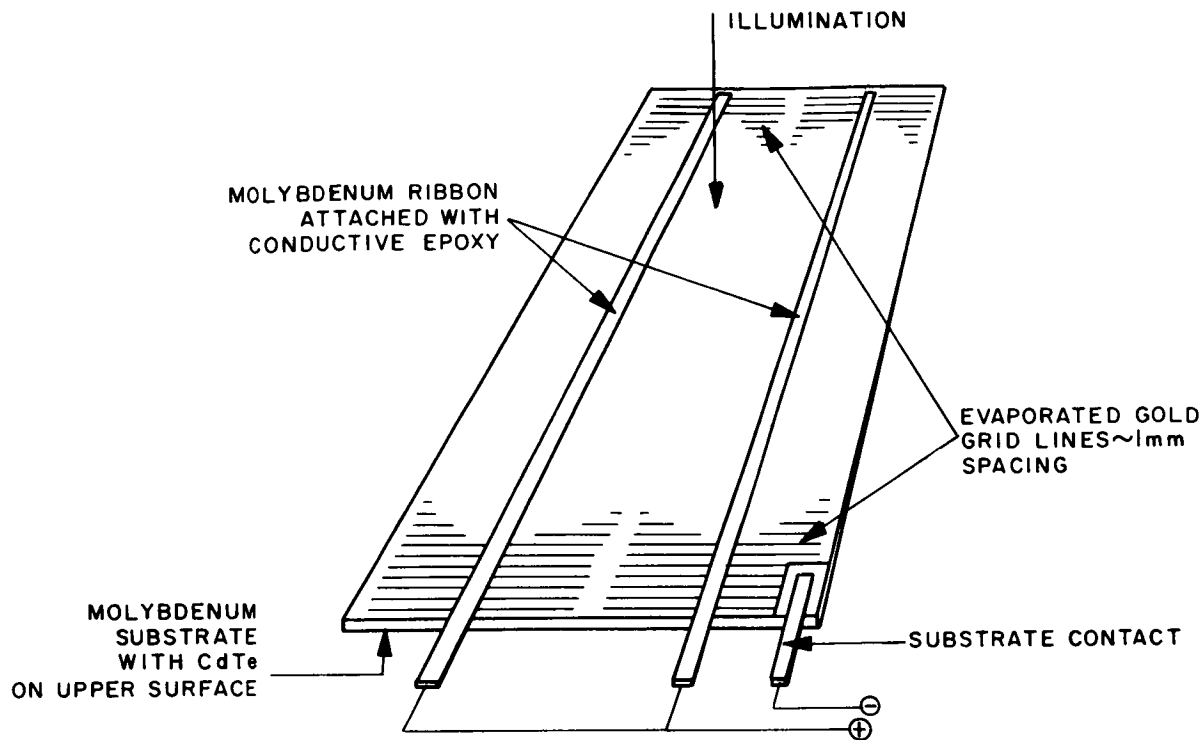


Figure 80. A two-by-four-inch thin-film CdTe solar cell on molybdenum substrate, circa 1964.

ideal, particularly since it would darken under UV irradiation, and did not provide complete moisture protection. A surprising result of this testing was that the various formulations of glass polymers and silicones were found to be quite unsuitable for cell encapsulation, the glass polymers failing on thermal-cycling to low temperatures, and the silicones providing very little moisture protection.

Radiation resistance measurements were made on a limited scale. The results showed that ^{60}Co radiation to a dose of 1.6×10^{17} Rad, and 2×10^{14} 5 MeV electrons cm^{-2} , produced no measurable degradation. 7×10^{13} 2.4 MeV protons cm^{-2} produced an average I_{SC} loss of 15.4%, although the results were very variable. It would be expected that these cells would be comparatively resistant to radiation, since the minority carriers seem to be created in a narrow region with a high field, and hence do not depend on long diffusion lengths for efficient collection. The experimental results supported this belief to a limited degree, although the variability of the proton irradiation results indicated a lack of uniformity in the cells which might be considered potentially troublesome.

During the period 1962-1965, a group at Harshaw Laboratories, led by Heyerdahl, also worked in the area of thin-film CdTe cells (446). Although this project ran for three years, it was only in the last year that attention was focused exclusively on CdTe. Various methods were used for forming the CdTe layers, including vacuum evaporation of the compound, vacuum evaporation of the separate constituents to react on a heated substrate, and vapor transport from the compound. The best results were obtained with the second of these, and most of the cells were made by this technique. However, variable and non-uniform electrical properties were obtained in the resulting films, and it appears that adequate process control was not achieved. The substrates used were molybdenum, and it was found that adequately low contact resistance between substrate and CdTe could be obtained only by the use of an intermediate layer. Various metals were tried for this layer, all of which gave inadequate CdTe adhesion. However, In_2Te_3 formed by coevaporation of In and Te was found to give adequate electrical and mechanical results, and this was used as a substrate precoat throughout the third year, when most of the cells were made.

Barriers were made by the cuprous ion dip process (as for the GE cells), and various studies were made to determine the details of this reaction and its products. Contact to the barrier layer was by pressed gold mesh.

However, good cell efficiencies were apparently never obtained during this work. The final report gives no details of efficiency measurements, but the I-V curves given for small-area (1 to 2 cm^2) cells indicate values below 1%. Low values of all cell parameters (V_{OC} , I_{SC} , and F) were indicated, and it appears that these disappointing results were largely due to a lack of control of the CdTe film deposition process.

Work at GE continued during 1965, 1966 and 1967 with USAF funding (447-449). During this period, major emphasis was placed on producing quantities of cells sufficient for array fabrication and large-scale testing, in addition to the experimental work aimed at increasing cell efficiency and stability. With the former objective in mind, a pilot production facility was established at GE Semiconductor Products Department at Lynchburg, Virginia, while the experimental work continued to be pursued at GE Research and Development Center, Schenectady, N. Y., and at the Electronics Laboratory, Syracuse, N. Y.

Experimental work aimed at developing more efficient and stable cells included:

- a. The investigation of single-crystal CdTe cells made with dopants other than copper: As, Sb, P, and Bi were used. Although working cells were made with As and Sb, it was not found that better thin-film cells could be made this way, and the cell manufacture continued to use the cuprous ion dip process.

- b. Various alternatives to the use of heavily-doped CdS as a substrate precoat to give low substrate/CdTe contact resistance were tried, with variable results. A precoat of vacuum-deposited copper was found to be effective, improving CdTe layer quality and increasing both V_{OC} and I_{SC} to give an efficiency improvement of 20%. Some cells with even higher efficiencies were obtained with molybdenum substrates treated with $AgNO_3$ solution to give a silver coating, but the results in this case were patchy. Although the most efficient thin-film cell made was obtained on a $AgNO_3$ -treated substrate (6% efficiency in a 1.8 cm^2 cell), the results were not sufficiently reproducible, especially when applied to the larger-area ($1'' \times 4''$) production-type cells, which continued to use the CdS substrate precoat at this time. However, a cost reduction in this latter process was obtained by replacing Ga doping of the CdS with $CdCl_2$ doping, to produce the necessary low resistivity.

Attempts were made to increase I_{SC} without reducing V_{OC} by making cells of $Cd_{1-x}Hg_xTe$ alloy. These attempts were not successful, and neither was a similar idea, the inclusion of Sb in the films to give impurity absorption of the unused low-energy photons below the CdTe band edge.

In many ways, the most pressing problem at this time appeared to be again that of cell stability. Hence a major effort was made to develop a cell coating technique which would prevent moisture penetration. Inorganic coatings were studied, particularly SiO , SiO_2 , TiO_2 , and Al_2O_3 . Much the most promising results were obtained with Al_2O_3 , which was deposited on the cells by vacuum evaporation using an electron-beam heated boule of sapphire as the evaporant source. About 1500Å min^{-1} deposition rates were obtained, and a film thickness of about 1500Å was used, to provide cells with a quarter-wavelength antireflection coating giving a deep blue coloration. Efficiency improvements of up to 20% were achieved, arising from I_{SC} increasing with the reduction of optical reflection. However, special care had to be taken to avoid the rise of the cell temperature above 120°C ; as with the earlier experience with SiO_2 coatings, this cell heating problem resulted from high source temperatures needed to evaporate these inorganic coating materials. However, cell temperatures above 100°C were found to aid in obtaining an alumina layer which would give a moisture-resistant cell.

The pilot line production facility established at Lynchburg started operation with the process steps developed earlier by the laboratories:

- a. 1 or 2 mil thick Mo substrates were coated with $0.5\text{--}1.0\text{ }\mu\text{m}$ of high-conductivity n-type CdS, made by introducing Cd powder and H_2S into the same reactor vessel as was used for CdTe layer growth. Later in this contract, a thin layer of copper was substituted for the CdS.

- b. CdTe films 10 μm thick, n-type, were deposited using the reactive vacuum deposition process with elemental Cd and Te, and CdI_2 (dopant), as starting materials. The top 2 μm (approximately) of the deposited layer was graded in doping by adding CuCl to the evaporant in the last stages of CdTe layer growth.
- c. Barrier formation was accomplished by dipping in CuCl solution at 85° C for 18 sec, forming a Cu_2Te layer.
- d. Barrier layer contact was made either by vacuum deposited Au grid (for the large-area cells) or with Ni mesh applied with transparent tape (for small-area test cells).

The standard production cells were 1" x 4", giving a 25 cm^2 nominal cell area, and efficiencies were 3.5% initially, increasing to 4-5% by early 1967.

During late 1966 and early 1967, processes for the fabrication of an integrated array of CdTe cells were developed. The approach involved attaching molybdenum substrates, after completion of the high-temperature processing, i.e., the CdTe film grown, to Kapton plastic film, and then using a sequence of etching and metallization steps to isolate cell segments and provide all cell electrical connections simultaneously. Efficiencies of about 3% were achieved by early 1967 using this approach, the arrays consisting of six cells series connected to give a total area of 8.75 cm^2 . In addition, deployable arrays fabricated with standard (1" x 4") cells were demonstrated, but this work will not be described here.

Cell stability continued to be an active area of investigation, and variable results were obtained. Extended shelf life testing showed low degradation rates in some cells, the I_{sc} dropping at a rate of 0.36% per month. This test was made on cells with Krylon coatings, stored for 32 months under laboratory ambient conditions. In addition, a small number of cells were made with the Cu_2Te barrier layer replaced with a semi-transparent platinum film. These cells showed efficiencies up to 4%, and gave indications of being stable even at 125° C.

The GE work is continuing, still with USAF funding (450). The latest contract, under which work started in early 1967, has as one of its primary objectives the reduction of cell mass, to a value of 0.02 lb. ft^{-2} . This has necessitated the investigation of lightweight substrates and the use of CdTe layers 5 μm or less in thickness, in place of the previously used 10 μm . Substrates investigated have been thinner molybdenum (0.5 mil versus the previous of 1.0 mil), titanium, and aluminum. While the aluminum is good from the mass and availability viewpoints, it has a coefficient of thermal expansion greatly mismatching that of CdTe, which may lead to problems of cell stability and mechanical integrity on temperature cycling. In addition, it has not been found possible to make cells with good efficiencies on this substrate material. The reason for this latter problem has not been stated, but the achievement of low-resistance ohmic contact between aluminum and CdTe is likely to be a problem. With titanium substrates,

reasonable cell efficiencies have been obtained, but adhesion between CdTe and substrate has been poor. Thin molybdenum foil has given the best results so far, the thinnest commercially available foil (0.5 mil) having been used as starting material for reduction to 0.2-0.3 mil thickness by chemical etching. By using these thin Mo foil substrates, together with thinner CdTe layers and evaporated grids, specific masses as low as 0.022 lb ft^{-2} were achieved in mid-1967, for small-area (6.5 cm^2) cells. Although the efficiencies of these cells were not as high as those obtained earlier with thicker CdTe layers (maximum of 3.6%), cell power-to-weight ratios of 140 W.lb^{-1} were achieved.

Reduction of the CdTe film thickness was found to result in the diode characteristics of the cells having a "leaky" reverse characteristic, and correspondingly low efficiency. However, it was found that this effect was strongly dependent on the substrate preparation process, leading to the belief that the problem could be solved by the development of a suitable substrate treatment. In addition, it was found that the reverse leakage could be largely eliminated, and the efficiency correspondingly improved, by reverse biasing the cells for a period of about an hour. However, this process has been found to be applicable only to cells with mesh grids (not vacuum-deposited grids), and to give cells which degrade to the original leaky state on storage.

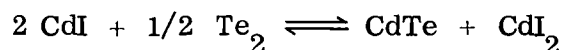
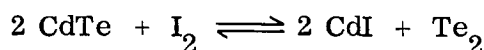
Various process improvements have been investigated including the development of an improved CdTe deposition system and the use of a phosphorous-doped surface layer in place of the Cu_2Te layer to provide the active CdTe junction; however, the P-doped cells did not show photovoltages. The new deposition system has involved the construction of a new type of reactor chamber, in which a single powder feed is used, the powder being a mixture of elemental Cd and Te. This process was investigated by Cusano in 1964, and rejected at that time because it was found that the compound CdTe was formed before volatilization of the components, and the reactor was not at a sufficiently high temperature to evaporate the CdTe once it was formed. However, new work will use a higher vaporization chamber temperature. In addition, a rotating substrate holder will be employed, which, it is hoped, will lead to more uniform electrical properties and thickness in the CdTe films.

Still more tests on coating materials have been run recently, with the conclusion that the Krylon coating first used in 1964 is still the best available encapsulant. Life tests in which cells were operated under low vacuum ($5 \mu\text{m}$ pressure) with tungsten illumination showed that normal cells underwent a degradation of efficiency to 34% of initial output after 95 days. However, cells which had been subjected to a $90^\circ\text{C}/4$ hours post-fabrication heat treatment showed less degradation (to 53% of initial output). Various other process variations, including substrate precoat and junction formation steps, are being evaluated in an effort to improve the stability. Although the conditions of the test are fairly rigorous, they are representative of what is to be expected in space operation of cells, and the amount of degradation seen must continue to be a worrisome aspect of CdTe thin-film cells' performance. This will no doubt be a major area of effort in the continuing work at GE.

Russian work on CdTe thin-film cells was reported by Landsman and Tykvenko in a paper submitted in early 1965 (451). This appears to have been principally an effort to duplicate the work of the GE group, since the CdTe layer deposition process and the barrier formation method were identical with those published by Cusano. The I-V characteristic given in the Russian report shows a fill-factor of 0.25 (i.e., a linear characteristic), thus R_s was severely limiting the performance of the cells. However, the family of characteristics shown for different illumination intensities indicates R_s decreasing linearly with intensity, implying a photoconductive effect which has apparently not been reported by Western workers. It is stated that 3.5-4.0% efficiencies have been achieved in the Russian work, for 1 cm^2 cells, with fill factors of 0.5-0.65, but the I-V curve for one of these better cells was not shown. Further reports of Russian work in this field have not been found.

French workers have recently shown an interest in CdTe thin-film cells. Rodot's group at C.N.R.S. reported results obtained with devices similar to those of Cusano, in 1966 (452). The cells were made by vacuum deposition of CdTe, starting from the compound, on aluminum-coated substrates (the substrate base material was not reported). The CdTe base layer was In-doped n-type, and a thin layer ($1 \mu\text{m}$) of high-resistivity CdTe was vacuum-deposited on its surface. This was followed by a film of Cu_2Te (100\AA), also deposited by vacuum evaporation, and finally by an evaporated copper grid. A heating cycle ($250^\circ \text{C}/30 \text{ min.}$) was found to improve cell performance by increasing I_{sc} and reducing leakage conduction. This heating step presumably forms a graded impurity concentration through the high-resistivity CdTe layer region, to give a band structure similar to that proposed by Cusano and illustrated in Figure 79. The French group reported diode characteristics, spectral response, and capacitance-voltage measurements, all of which could be analyzed in terms of the proposed band structure. Although single-crystal cells prepared with these barrier formation steps showed efficiencies up to 5%, the thin-film cells were all below 1% efficient because of high series resistance.

Piaget, also working at a French government laboratory, reported a method for forming CdTe layers which would be applicable to CdTe solar cells (453). This involved an iodide transport reaction:



previously described by Alferov (345). Whereas the Russian work was done in ampoules sealed under vacuum, Piaget used an ambient of hydrogen or a noble gas at atmospheric pressure. Photovoltaic cells were made from CdTe layers deposited by this process onto molybdenum substrates, using a vacuum deposited Cu_2Te barrier layer, and gold grids. These showed efficiencies up to about 1%, being limited in performance by high R_s values.

In 1967, Rodot reviewed work on CdTe thin-film cells (454), and discussed the mechanism and band structure of the cells. He concluded that they could contain either a p-Cu₂Te/n-CdTe heterojunction, or a p-CdTe/n-CdTe homojunction with Cu₂Te making ohmic contact to the p-CdTe, depending on the conditions of cell preparation. This conclusion is very much in agreement with the results of the GE group in considering this question.

Further French work in CdTe thin-film cells was done at the laboratories of Société Anonyme de Télécommunications et la Radiotechnique, and reported in 1966 (455). The cells were made on CdTe films deposited by the GE method, also on CdS-coated Mo substrates. However, barrier formation was tried not only by the cuprous-solution dip process, but also by the vacuum-deposition of Cu₂Te. Most cells were in fact made by the latter process, and gave efficiencies up to 3%, with $V_{OC} = 0.4 - 0.5$ V, and $I_{SC} = 7$ mA cm⁻², under 50 mW cm⁻² sunlight. This low illumination intensity would reduce the effects of series resistance, but the results obtained indicate that the vacuum deposition of Cu₂Te is a usable alternative to the dip process. Results of this group were also quoted by Rodot, who indicated that cells of 36 cm² area had been made with efficiencies up to 4%, by using flash evaporation to form the Cu₂Te layer. Further reports of progress by this group have not been found.

This completes the historical account on CdTe thin-film cell development. The GE groups have been providing by far the largest effort in this field, and the degree of their success in solving the stability problem and improving the conversion efficiency, can be expected to determine whether or not this type of cell will find application in the future.

4. Gallium Arsenide

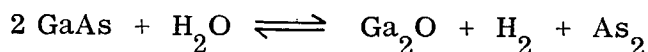
As far as can be determined, the only work in the U.S. aimed at developing thin-film GaAs solar cells was done at RCA Laboratories under P. Rappaport, during the period October 1962-August 1967. Two projects were supported by research contracts with the NASA and USAF, and the chronology of these is indicated in Table XX.

The initial impetus to investigate this type of cell arose from three factors:

- a. The work of Loferski had shown that the band gap of GaAs matched well with the solar spectrum, so that the potential efficiency of such a cell was high.
- b. GaAs was known to exhibit a large optical absorption constant for photons with energy exceeding E_g , i. e., it was known to be a direct bandgap conductor, and it should therefore be suitable for thin-film cell use.
- c. Methods for making thin layers of GaAs had been developed to the point where they could be applied to the fabrication of experimental cells.

In fact, however, the available methods for growing the GaAs films were not easy to control, and investigations aimed at learning about these processes were the primary interest during the early work (456) carried out under NASA funding.

Various GaAs layer growth processes were evaluated initially, including transport by thermal gradient in a sealed tube, growth from solution in Ga liquid, halide and hydrogen vapor transport, and oxide transport. The latter proved the best, and was used extensively in all subsequent work. The process was known to involve a reversible chemical reaction:



The Ga_2O and As_2 were volatile at the source temperature (about 750°C), and the reverse reaction occurred on the substrate (700°C). The GaAs source was a wafer of single-crystal or polycrystalline GaAs, and the process was usually run with the source parallel to the substrate, spaced from it by a few millimeters. The source wafer was maintained at a higher temperature than the substrate, the forward reaction in the equation being favored by higher temperatures. The furnace ambient was hydrogen, to which a small proportion of water vapor was added to supply oxygen and thus act as transport agent in the reaction. It was found that control of the GaAs layer conductivity type could be obtained by using source GaAs with an appropriate dopant, together with controlled operating temperatures and water vapor (oxygen) concentration, although n-type material was easier to obtain than p-type.

GaAs layers were grown on tungsten, molybdenum, and quartz substrates with various pretreatments (coatings of germanium, manganese, or aluminum) to increase the nucleation site density. The best thermal expansion match was obtained with molybdenum, which remained in general use for much of the subsequent work.

Initially, cells were made by growing GaAs layers with change of conductivity type (both n-on-p and p-on-n cells were made) and photovoltaic action was observed in these structures, though the junctions were of poor quality. Diffusion methods for forming the junction were also studied, but it was found that leakage along the grain boundaries in polycrystalline material caused both the diffused-junction and grown-junction characteristics to be poor. Hence alternative cell types were investigated.

One of the available alternatives was the use of a surface barrier in place of the p-n junction to form the active region. (An account of the rectifying action of this type of surface barrier has been given in Sections II-C, and III-D-2 above). The surface barrier material would have to provide optical transmission for the majority of incident photons in the response range of the cell, as well as being electrically conductive. In addition, it would have to interact with the GaAs surface in such a way as to give the required band structure, as shown in Figure 21. The barrier material could either be a metal which formed a set of surface states leading to the formation of an inversion

layer by the processes discussed by Bardeen, or it could be a p-type semiconductor which would form a heterojunction with the n-type GaAs. In the latter case, the band structure would be as shown in Figure 81 if the p-type semiconductor were degenerate, as it has been in practice in thin-film cells. One notes also that the barrier layer material should be chosen to give surface states leading to the maximum value of E_B (in principle this could be E_g at the most), since this determines V_{OC} for a cell made this way.

Barrier layer materials investigated included vacuum-deposited copper, Cu_2S , and $ZnTe$, as well as layers of CuI , Cu_2S , Cu_2Se , Cu_2Te , NiS , and CdS formed by electrodeposition of the metal followed by chemical reaction with a vapor or solution of the iodine or chalcogen to give the compound. The results of these experiments are summarized in Table VI. By late 1963, cell efficiencies of 1.4% had been obtained in devices of $6 \times 10^{-2} \text{ cm}^2$ area, with copper or Cu_2S barriers.

A novel cell structure was also investigated during early phases of the work. This was based on an aluminum substrate into one surface of which a layer of fine GaAs particles was impressed. The soft aluminum surface held the GaAs, and the remaining exposed surface of the substrate, in the interstices between the particles, was anodized to provide electrical isolation. Application of a barrier to the exposed surface

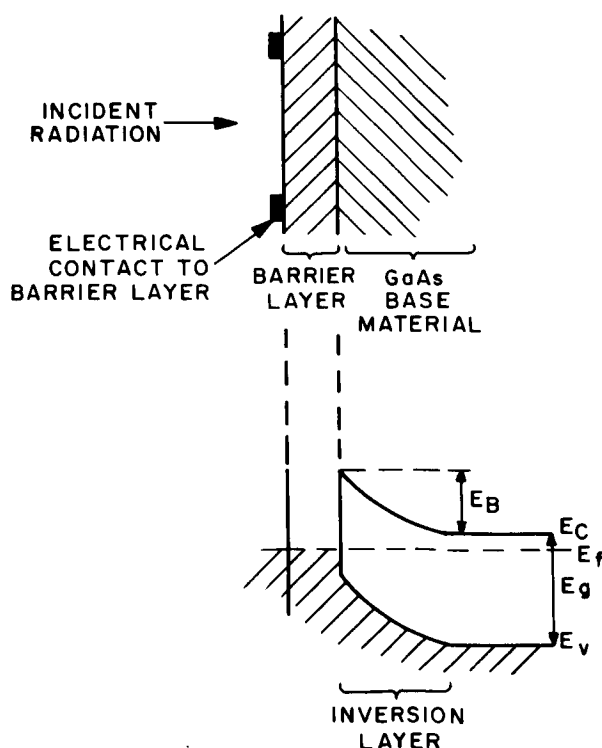


Figure 81. Cross-section and band structure of the active region formed by a barrier-layer contact to a semiconductor surface.

TABLE VI. SUMMARY OF RESULTS WITH VARIOUS BARRIER-FORMING MATERIALS ON GaAs

Material	Fabrication Method	Result
Cu	Electrodeposited on polycrystalline GaAs	High leakage and high series resistance
Ag	Electrodeposited on polycrystalline GaAs	Low photoresponse
Al	Vacuum evaporated	Low photoresponse
CuI	Electrodeposited Cu, exposed to I vapor, on single-crystal GaAs	$V_{oc} = 0.79V$, sheet resistance increases with time
Cu_2S	Electrodeposited Cu, reacted with H_2S or S in CS_2 , or vacuum evaporated	$V_{oc} = 0.6V$, sheet conductivity-transmission product low
Cu_2Se	Electrodeposited Cu, reacted with Se in benzene, or vacuum	$V_{oc} = 0.75$, stable film
Cu_2Te	Electrodeposited $TeBr_4$ reacted with $CuSO_4$, also vacuum evaporated	$V_{oc} = 0.6V$, high sheet resistance, high shunt conductance
CdS	Electrodeposited Cd exposed to H_2S or anodized in $(NH_4)_2S$ soln., on single-crystal GaAs	No photovoltage on n-type GaAs
ZnTe	Vacuum deposited with Cu dopant on GaAs single crystal	$V_{oc} = 0.43V$
In_2O_3	$InCl_3$ sprayed onto substrate at $350^\circ C$ in air	Transparent films, sheet resistance $< 100 \Omega sq^{-1}$, ohmic contact
Bi_2O_3	Vacuum evaporated	$V_{oc} = 0.15V$
MoO_3	Vacuum evaporated	Sheet resistance $> 10^8 \Omega sq^{-1}$
NiO	Decomposed on evaporation	-
PbO	Decomposed on evaporation	-
NiS	Decomposed on evaporation	-
SnS	Vacuum evaporated	Sheet resistance $10^7 \Omega sq^{-1}$ small photovoltage
Cu_3P	Vacuum evaporated	$V_{oc} = 0.4V$
SnO		Low photoresponse
NiS	Electrodeposited Ni reacted with H_2S , on crystal GaAs	$V_{oc} = 0.35V$

of the GaAs particles would then create a cell in the desired thin-layer geometry. (The entire approach closely resembles that investigated at Hoffman Electronics for the fabrication of large-area solar cells using silicon spheres.) Initial evaluation of the electrical characteristics of GaAs pressed into aluminum foil indicated that a high contact resistance existed: pre-coating the foil might have eliminated this problem. However, the packing density of the particles on the substrate could not be expected ever to exceed 70% of area utilization, so that when more promising approaches to cell fabrication appeared, this work was discontinued.

A parallel USAF-funded project also was running at this time at RCA, and a portion of the effort under this contract was directed towards investigating GaAs thin-film cells (322). The greater part of this work was directed towards making epitaxial layers of GaAs on single-crystal Ge substrates, this being a possible cost-cutting method, since it would avoid the necessity for using single-crystal GaAs wafers in making GaAs cells. To obtain an ohmic Ge/GaAs contact, it was found necessary to use Ge with very low resistivity (2×10^{-3} ohm-cm.), and 20 mil thick n-type wafers were found to provide the best results. Onto these substrates, n-type GaAs films 2-4 mils thick were grown. Various GaAs growth processes were used, based on vapor transport in a hydrogen gas stream from a GaAs source, or reactive transport using separate Ga and As sources with hydrogen or bromine as the carrier gas: the reader is referred to the original reports for process details.

Junctions were formed either by Zn diffusion using methods developed under the RCA single-crystal GaAs solar cells program (see Section IV-C-1 above), or by growing successive n- and p-type layers by changing the dopant during film growth. After junction formation, a surface etching process was used to reduce the surface region thickness, again a step developed during the single-crystal GaAs cells work.

The performance of the best thin-film GaAs cell is compared in Table VII with that of a bulk GaAs single-crystal cell made simultaneously. This simultaneously prepared single-crystal cell acted as a control with respect to the influence of process parameters (such as active junction formation) which were common to both types of cell.

The degrading effect of R_s on the fill-factor is particularly apparent, and V_{oc} is also noticeably poorer in the thin-film cell.

Further work on the formation of thin-film GaAs cells on Ge substrates appears to have not been done. Although methods for the growth of epitaxial GaAs layers have made major advances in recent years (458), these high-quality processing techniques require exacting control, and cells made in this way appear unlikely to become cost-competitive with the present Si solar cells. In the particular case of these thin-film GaAs cells made on single-crystal Ge substrates, the major advantages of thin-film cells (elimination of the crystal growth step, large area devices, low weight, and flexibility) would not be obtained, which probably accounts for the lack of further interest in this type of device.

TABLE VII. COMPARISON OF PERFORMANCES OF THIN-FILM AND BULK GaAs SOLAR CELLS

Performance Characteristic	GaAs/Ge Cell	Bulk GaAs Cell
Efficiency (%)	3.2	7.3
V_{oc} (V)	0.74	0.89
J_{sc} (mA.cm ⁻²)	8.3	10.5
F	0.52	0.78
Area (cm ²)	~0.1	0.12

However, a second area of activity during this contract (322) proved to have greater promise. Cells were made by forming surface barrier contacts to GaAs using evaporated thin films of various metals, including aluminum, silver, gold, copper, chromium, palladium, and platinum. Contacts were deposited onto bulk single-crystal GaAs, epitaxial GaAs on Ge substrates, and polycrystalline GaAs on molybdenum substrates, all GaAs having n-type conductivity. The aluminum layers were found to give ohmic contacts, while the other three metals gave rectifying contacts, with platinum having the greatest barrier height (E_B in Figure 81). The photovoltaic behavior of these Pt-GaAs contacts was measured, V_{oc} being found to increase with reduction of carrier concentration in the GaAs. This was explained by the widening of the depletion region, which resulted in reducing the amount of tunneling through the junction. (Such tunneling may account for the excess current seen in p-n junctions, as discussed in Section IV-A-2 above.)

Efficiency measurements were made on cells which had been prepared by depositing semi-transparent layers of Pt on GaAs, a semitransparent overcoating of Au being added to reduce the series resistance which would arise from the lateral resistance of the Pt film. Cells were made on single-crystal bulk GaAs, epitaxial GaAs on Ge single-crystal substrates, and polycrystalline GaAs on molybdenum substrates. With the GaAs/Mo cells, efficiencies up to 3% were achieved in operation under 75 mW cm⁻² sunlight, with $V_{oc} = 0.64$ V, $J_{sc} = 8.7$ mA cm⁻², on a cell of 0.19 cm². A considerable series resistance loss was present in this cell, the fill factor being only 0.39.

This resistance was believed to arise at the contact between the molybdenum substrate and the GaAs layer. It was also found that photovoltaic performance could be achieved only for polycrystalline layers with thickness greater than about 3 mils, best results being achieved with GaAs thicknesses in the 4-5 mils range. Thinner GaAs layers were found to lead to leaky or shorted diode characteristics. This promising start was followed up some time later (see Table XX). In the intervening period, late 1963 to 1964, however, the NASA-sponsored work continued alone.

Following the barrier-material evaluation experiments carried out during the first contract, work was concentrated on the copper sulphide barrier layer system, and, during 1964 considerable development effort was put into forming thin films of this material (457).

Vacuum evaporation was employed for forming the films, with a fresh charge of Cu_2S being used for each evaporation. The films as immediately prepared showed a resistivity of 200 Ohm cm; however, the resistivity dropped on exposure to air. A very much more striking decrease in resistivity was obtained when the film was exposed to the vapor over ammonium polysulfide, resistivities of 6.5×10^{-4} Ohm cm being obtained. The optical transmission of the films was measured as a function of wavelength, and from these measurements and the conductivity results it was concluded that the deposited films absorbed sulfur during the vapor treatment, to form copper vacancies, thus increasing the electrical conductivity, Cu_2S being a deficiency semiconductor. I-V measurements on Cu_2S films deposited on single-crystal GaAs wafers indicated that the contact behaved electrically like a metal-semiconductor junction, confirming that the Cu_2S was degenerate.

Cells made with Cu_2S exhibited 1.5% efficiencies over areas of 0.72 cm^2 , with $V_{oc} = 0.5$ volt. The main efficiency limitation was found to be cell resistance, which severely degraded the fill-factor.

The initial survey results also indicated that cuprous selenide Cu_2Se was a potential alternative to Cu_2S , so a development effort was made with this material. The vacuum evaporation technique evolved from this effort yielded films of 175-Å thickness, which were 70% transmitting for 1.5 eV radiation and gave a sheet resistivity of 93 Ohm per square. Not only was this result encouraging, but thin-film GaAs cells on Mo substrates subsequently made with cuprous selenide as a barrier layer gave indications of efficiencies close to 4% over small areas.

It was found necessary to coat the molybdenum substrates with a thin layer of tin to obtain low Mo/GaAs contact resistance. In view of the rather high weight penalty involved in the use of molybdenum as a substrate material, the use of aluminum foil for this purpose was also investigated. This necessitated the use of substrate temperatures below 640°C (to avoid melting the aluminum), which in turn limited the GaAs source temperature and hence the film growth rate. Nevertheless, working cells were made with GaAs layer thicknesses between 5 and $10 \mu\text{m}$. The efficiencies of such cells were only about 0.1%, because of high series resistance arising at the Al/GaAs interface. However, it was felt that the potential for making very light-weight cells would justify further work with aluminum substrates.

During 1964, two approaches to achieving GaAs film growth under vacuum were investigated. These were flash evaporation and sputtering, and both gave similar results.

The sputtering deposition system used as the source material GaAs wafers, which were mounted with conducting epoxy cement on a tantalum sheet. Typical deposition conditions were:

Discharge current	10 - 15 mA
Voltage	1900 - 2300 V
Argon pressure	$5.5 - 6.5 \times 10^{-2}$ Torr
Substrate temperature	250 - 600°C
Cathode-substrate distance	3 cm
Deposition rate	$160 - 240 \text{ \AA min}^{-1}$
Argon flow rate	$1 - 3 \text{ ml min}^{-1}$

The argon was passed through a desiccant before use.

The flash evaporation system employed particles of GaAs 10 to 14 mils in diameter, which were fed into a tungsten boat heated to 1600°C. The vacuum during deposition was the order 10^{-5} Torr, and most films were grown at about $1000 \text{ \AA min}^{-1}$. Substrate temperatures between 200 and 600°C were used, and GaAs films were successfully grown on glass, molybdenum, single-crystal GaAs, vapor-grown layers of GaAs, and calcium fluoride.

Results from both methods showed that amorphous films were obtained on substrates at room temperature, and that crystallinity in the deposits increased with increase of temperature. Single-phase GaAs was in general obtained, as evidenced by X-ray diffraction studies.

Measurements showed that the films obtained at low substrate temperatures had anomalously high optical absorption for wavelengths longer than the band edge, compared with single-crystal material. With increasing substrate temperatures, this anomalous effect became less pronounced, but even the best films did not show the sharp absorption edge and low long-wavelength absorption characteristic of single-crystal material. In this respect, vapor-grown GaAs layers showed behavior much closer to bulk single-crystal material. The optical properties of the vacuum-deposited layers were not of direct significance, but were an indication that the film material differed considerably from bulk and vapor-deposited GaAs.

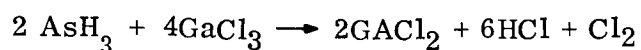
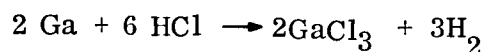
If not intentionally doped, the vacuum-deposited films were p-type. To produce n-type material, high doping concentrations (0.1 to 1.0% Sn) were found to be necessary. Undoped p-type films exhibited resistivities of 10^3 to 10^5 Ohm cm. Heavy doping with manganese (more than 0.1% Mn) reduced the resistivity of the p-type films to between

10 and 10^3 Ohm cm, but n-type films always had resistivities of 10^4 to 10^6 Ohm cm. Some evidence for a correlation between increasing substrate temperature and higher resistivity was found. These electrical measurements definitely indicated that the vacuum-deposited GaAs would be unsatisfactory for cell fabrication. These results all correlated with those published by other workers (459).

Continued support was obtained from NASA during 1965 (460, 461) and work was concentrated on cells made with cuprous selenide barriers. Both molybdenum and aluminum substrates were used, and the substrate/GaAs contact resistance problem was tackled. The tin precoat layer for molybdenum previously determined to be beneficial in reducing the series resistance, was found to lead to high carrier concentrations in the GaAs film, apparently because of tin spreading throughout the GaAs during the growth process. To inhibit this effect, a diffusion barrier consisting of a thin film of germanium was added to the precoat process, forming the sandwich structure Mo/Sn/Ge/GaAs. Using this process, cells on molybdenum substrates were made with efficiencies up to 4.6% for areas of 0.03 cm^2 .

The Ge-Sn precoat was not found to be applicable to GaAs on aluminum substrates, however, but for these a thin layer of InSb was found to form a satisfactory intermediate layer between GaAs and aluminum. The InSb was deposited by a vapor transport process similar to that used for the GaAs. Initial work with aluminum substrates was done with $25\text{-}\mu\text{m}$ -thick foil, but this material curled after the GaAs layer had been grown on it, presumably because of the coefficient of thermal expansion mismatch between substrate and GaAs. With thinner foils, however, the problem was less severe, and with the thinnest foil which could be handled satisfactorily ($5 \mu\text{m}$) no curling was seen. This result was presumed to be due to the ability of the aluminum to yield plastically when used in such a thin section. By mid 1965 cells with the structure Al/InSb/GaAs/ Cu_2Se were made with efficiencies up to 4%, for areas of 0.03 cm^2 . These cells on aluminum substrates were found to degrade on storage in air, losing I_{SC} and fill factor over a period of days or weeks. The results were found to be highly variable, but experiments indicated that the cells made with a final etch step in dilute acid after the formation of the Cu_2Se film were much less prone to this degradation.

Methods alternative to the oxide transport process, using single-crystal GaAs source wafers for making the GaAs films, were also investigated during 1965. One of these other chemical systems for forming GaAs layers is described by the reactions:



The first reaction is obtained by passing HCl (diluted with H_2) over the metal at about 700°C . The resulting vapor is mixed with arsine and passed over the substrate at 600 to 650°C , where the second reaction proceeds.

Equipment specially designed for use with thin metal foil substrates was built and operated. The design was such that InAs and GaAs films could be deposited sequentially (the reactions above are valid if In is substituted for Ga). Various difficulties with the equipment were encountered and solved, but cracking and curling of the aluminum foil substrate under attack by the HCl in the gas mixture proved to be a persistent problem. Some satisfactory films on small areas of the substrate were obtained, but the effort was discontinued to allow concentration of effort on other areas of research.

A method combining the principles of the vapor transport technique and halide transport system was also evaluated. Gallium was transported from the metal by the oxide reaction described above, and arsenic was introduced as arsine. Layers of GaAs were formed on molybdenum substrates, but difficulty was encountered in obtaining uniform deposits free of gallium precipitations. The work on this method was also discontinued.

By the end of 1965, work was concentrated on the aluminum-substrate cells, and efficiencies up to 4.3% had been achieved with cells of 0.73 cm² area. These larger devices necessitated the use of a collector grid to minimize series resistance effects arising from the sheet resistance of the Cu₂Se layer. Vacuum-deposited gold grids were found to be satisfactory. Cells with this structure gave a power-to-weight ratio up to 135 W.lb⁻¹, and some cells were stored for periods of up to 4 months under room ambient conditions without showing signs of degradation.

This work was followed up under NASA funding in 1966-1967 (462, 463).

Attention was focused on three problem areas:

- a. increasing the reproducibility of the fabrication process,
- b. increasing power conversion efficiency, and
- c. increasing cell dimensions.

The reproducibility of the GaAs deposition process had been found to be a major difficulty, but control of the gas flow rates and of the oxygen concentration in the furnances was found to yield the necessary results. Efforts to increase the cell efficiency by optimizing the InAs, GaAs, and Cu₂Se film thicknesses did not yield great gains in cell efficiency. However, coupled with the improvements in process control, average efficiencies were considerably improved, so that 3-3.5% were achieved by mid-1967 for 1 cm² cells, although the best cell efficiency obtained during this period (4.2%) was no better than results achieved earlier. The only major successful innovation aimed at efficiency improvement during this period, was the development of an anti-reflection coating of a 1/4-wavelength thickness of MgF₂, deposited by vacuum evaporation on top of the Cu₂Se barrier layer. However, this was developed too late to be applied to the majority of cells made under this contract.

Towards the goal to make larger-area cells, a furnace to accommodate larger substrates was built and operated. This furnace was based on the same oxide-transport process for growing GaAs films as that used for the 1 cm² cells. The films obtained showed nonuniformities which were believed to arise from temperature gradients and gas flow patterns in the growth region. Portions of the films grown were suitable for cell fabrication, but at no time was a layer of 10 cm² (the furnace capacity) obtained with uniformity adequate for the fabrication of a cell with this area.

A comprehensive stability testing program showed that cells stable under humid-air, vacuum, and oxygen environments, and operated for 2 months at illumination levels giving power outputs equivalent to 100 mW.cm⁻² sunlight, could be made using post-fabrication etching processes. Experimental results aimed at elucidating the degradation process indicated that this was due to the formation of a layer of copper oxide between the Cu₂Se barrier layer and the gold grid, and that the etching step which provided cell stability worked by altering the stoichiometry of the Cu₂Se layer to give the more stable Cu_{1.85}Se composition.

Reasons for the limited efficiencies of these cells were sought through analysis of the electrical properties of the Cu₂Se/GaAs junctions. It was concluded that the major difficulty lay in obtaining sufficiently small values of I₀, thus resulting in modest V_{OC} values (0.49 V) compared with those theoretically possible (1.0 V). In addition, various factors (optical reflection, absorption of photons in the barrier layer, and a minority carrier collection efficiency of about 90%) contributed to reduce the I_{SC} below the theoretical limit. A side result of measurements made during this efficiency analysis program was the fabrication of a barrier-layer cell using Cu₂Se on single-crystal GaAs, for which an efficiency of 8% was measured. This cell had a V_{OC} of 0.75V, I_{SC} of 9.65 mA, and a fill-factor of 0.575, and an area of 0.55 cm². These results may have interesting implications for potential fabrication of single-crystal cells made by this method.

In late 1964, USAF funding was obtained by RCA to pursue further the early results obtained with thin-film GaAs cells made with platinum barrier layers (461, 464). These cells were made on 2-mil thick Mo foil substrates, with a vacuum-deposited Ge-Sn precoat to give low Mo/GaAs contact resistance. The GaAs film was 4 mils thick, grown by the oxide transport process from single-crystal GaAs source wafers. The Pt barrier film was deposited by vacuum evaporation from a tungsten filament. A thickness of approximately 40Å, giving an optical transmission of 70% and a sheet resistance of about 1000 Ohms per square, was found to be optimum. A thin film of gold was deposited by vacuum evaporation over the Pt, to increase its electrical conductivity, and experiments showed that a thickness of 45Å was optimum for cells of small area (0.2 cm²). Antireflection coats of Krylon (applied from an aerosol spray), and SiO (deposited under vacuum), were used. The krylon also provided some protection against cell degradation by atmospheric effects.

In late 1964, efficiencies of 4.3% had been achieved in cells of 0.2 cm² area. By the end of this contract, 12 months later, the performance had improved so that 5.1% efficiency had been achieved in a 0.2 cm² cell, a 2 cm² cell had been made with an efficiency of 4.5%, and a 4 cm² cell with an efficiency of 3%. With these larger area cells, the Au film was replaced by a Au grid, formed by vacuum evaporation through a mask.

These cells had been etched in HCl after deposition of the barrier layer, a process which had been found to increase the conversion efficiency by improving V_{oc} . However, it was discovered that cells prepared with this final etching step exhibited a degradation on storage under room ambient conditions. Although the original performance could be restored by re-etching the cells, degradation would once again occur. Cells made without this etching step gave lower initial efficiencies, a maximum of 2.8% on a 2 cm² device having been obtained, but they appeared to be wholly stable.

Proton irradiation damage measurements were made on these cells, and a large loss in cell output was found for low energy protons: the results are shown in Table VIII.

TABLE VIII. EFFECTS OF PROTON RADIATION ON THIN-FILM GaAs CELLS

Energy (keV)	Flux (cm ⁻²)	Initial Values		Final Values	
		V_{oc} (V)	I_{sc} (mA)	V_{oc} (V)	I_{sc} (mA)
400	1.16×10^{14}	0.406	0.060	0.031	0.010
100	5.45×10^{14}	0.465	0.150	0.113	0.027
50	2.27×10^{12}	0.497	0.120	0.198	0.020

The loss in V_{oc} implies that I_0 for the junction was increased drastically by this irradiation, presumably through introduction of recombination centers in the surface and depletion regions of the cells. This would also degrade I_{sc} by reducing the collection efficiency. One might note, however, that high-energy electrons would be expected to do comparatively little damage to GaAs thin-film cells, because they do little damage within a diffusion length of the cell surface. This is because high-energy electrons have relatively great penetration into the cell, and thus the damage they do is distributed over a large volume of semiconductor material. In contrast, low-energy protons interact relatively strongly with the semiconductor, and thus they penetrate only a small distance into the cell, and the damage is localized near the cell surface.

The project continued to receive USAF support during 1966 (463, 465). Studies showed that it was not possible to eliminate the degradation problem with the etched Pt/GaAs barrier, and the modest V_{oc} values with unetched contacts prompted a search for

alternate junction formation processes. The use of a semi-transparent copper film in place of the platinum provided reasonably efficient cells, but these were found to degrade, presumably because of the comparatively reactive nature of the copper. Junctions were made by diffusing zinc into the GaAs to form a p-type surface layer, and although the improved quality of the GaAs enabled better results to be obtained than those seen three years earlier, it was still found that the results could not be controlled sufficiently well to give good cells. As before, junction leakage by excessive diffusion along grain boundaries was believed to be the cause of the difficulty.

In the absence of a better alternative, Pt/GaAs barrier layer cells continued to be made. Small increases in performance were secured, so that by the end of the contract cells were made of 2 cm² area with efficiencies up to 3.8%.

The structures of the two types of thin-film GaAs cells developed at RCA are compared in Figure 82. With both the Cu₂Se/GaAs cells on aluminum substrates and the Pt/GaAs cells on molybdenum substrates, there seemed little likelihood of quickly achieving performance levels to match those of the II-VI compound thin-film cells. Hence, in 1967, work on GaAs cells was discontinued.

Work aimed at developing methods for making thin-film solar cells has also been performed in France by a group at the government-support Laboratoire d'Héliotechnique (466). This was a continuation of research pursued earlier in another government laboratory in Algeria, which was terminated by the political events in that country

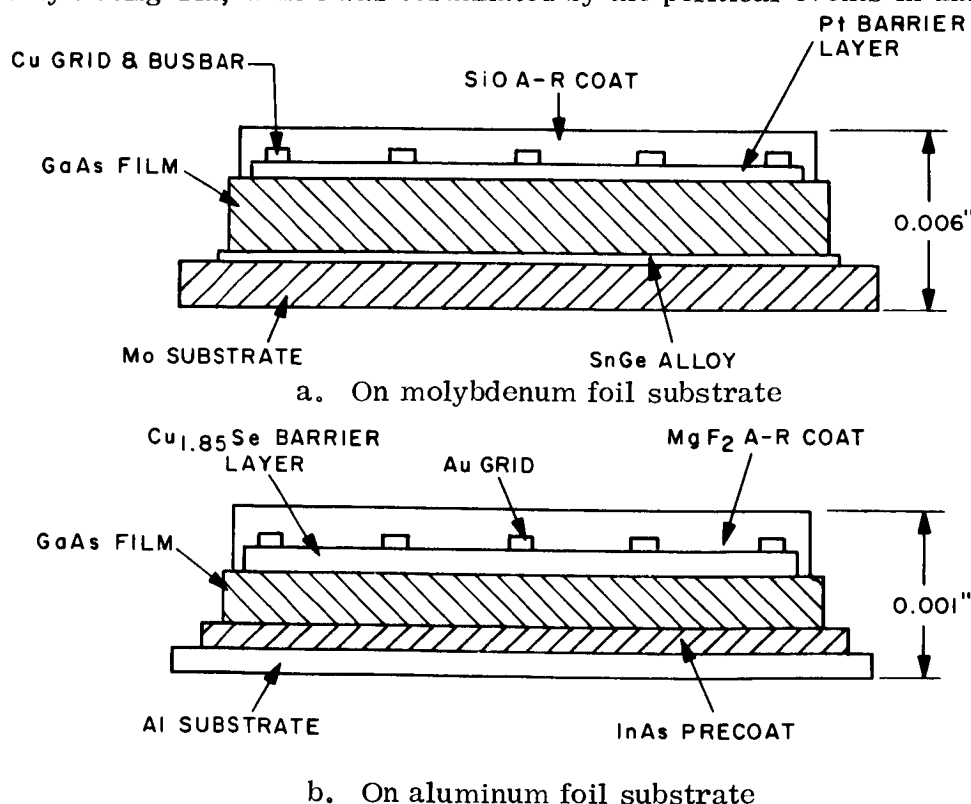


Figure 82. Thin-film GaAs solar cell structures in cross-section.

during 1964. GaAs was deposited on glass substrates using the three-temperature deposition process,²⁰ and on mica by flash evaporation. Measurement of the film properties indicated that at substrate temperatures approaching 470°C, crystalline GaAs was formed, but this material had very poor electrical properties. In particular, its resistivity was characteristic of the semi-insulating form of the compound, which was in agreement with results by the RCA group (460, 461) and others (459). It would not have been possible to make solar cells from material with these properties, and further reports of this work have not been found.

It is believed that there is no work in progress on GaAs thin-film solar cells at the time of writing. The reasons for the peculiar difficulties encountered in this work, and the contrast between III-V and II-VI compound semiconductor thin-film cells, will be analyzed later in this report.

5. Other Materials

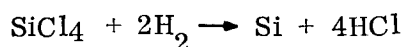
Exploratory work has been done on a few other materials for thin-film solar cells, but the results have been such as to discourage any major effort at cell production.

In spite of the difficulties anticipated in using silicon as a thin-film cell material, as described in the introductory paragraph of this section, various efforts have been made to fabricate such cells from this material. Attempts to grow thin sheets of silicon by the dendrite-web method, the float method, and the travelling-solvent method, lie closer to bulk silicon cells than to true thin-film solar cells, and an account of this work has been given in Section IV-B-3, above. One other thin silicon cell concept will be considered here, however, since it is more nearly a true thin-film cell.

Initially under internal funding, and later with Signal Corps support, a group at Honeywell Research center made thin-film polycrystalline silicon solar cells, during the period 1960-1964 (467, 468). Thin layers of silicon were formed by passing a

²⁰ For a full exposition on the mechanism, the reader is referred to Compound Semiconductors Vol. I, eds. Willardson and Goering (Reinhold, New York, 1962), Chapter 35. The method is applied to the deposition of compounds whose constituents have widely different volatility. The elements are evaporated from separate sources, at two different temperatures. The volatile species is evaporated at a rate providing an arrival rate over the substrate greater than that required to form the stoichiometric compound. The substrate is maintained at a temperature such that the vapor pressure of a separate phase of the volatile component would be enough to re-evaporate the excess, without being so high as to cause the desired compound to lose the volatile component. Clearly, the method is applicable only to those compounds for which the ratio of the vapor pressure of the volatile component over its own phase to that over the compound, is large. The "three temperatures" are those of the two separate sources, and the substrate.

mixture of silicon tetrachloride and hydrogen over a substrate heated to 1200-1300°C, a process well-established in the semiconductor industry for the growth of epitaxial silicon:



Phosphorous trichloride and boron tribromide were used to provide n- and p-type doping, respectively. Various substrates were used initially, including tantalum ribbon, and it was proposed that eventually a ceramic substrate should be used. However, most of the cells made contained silicon layers grown in a sufficient thickness to be self-supporting. These layers were formed on a graphite substrate heated by rf induction. The surface of the graphite was coated with a layer of soot, which acted as a "release agent," allowing the silicon layers to be stripped from the graphite. However, this process was not 100% effective, and difficulties were encountered in obtaining layers free from cracking. Consequently, a number of cells were made with silicon deposited onto silicon substrates.

Since the major objective of this program was to provide low-cost devices, the Honeywell group did a good deal of work to evaluate the dependence of the silicon quality on the use of the lower purity grades of reagents and gases. In addition, the effect of the grain boundaries in the polycrystalline material was also measured. The results indicated that thin-layer polycrystalline cells made with these low-cost methods could be expected to have efficiencies up to 5%.

Actual cells were made by depositing a layer of low-quality Si about 16-20 mil thick, followed by a higher-quality layer about 3 mils thick. The initial material provided mechanical support, and the upper region formed the active region of the cell. The junction was made either by changing the conductivity type of the silicon during the terminal phase of layer growth, or by regular diffusion processing as used for bulk single-crystal solar cells. Contacts were applied by the electroless nickel process.

By late 1963, cells with 3% efficiency for 6 cm² area were obtained, with J_{SC} values of 18 mA cm⁻². However, the difficulties encountered indicated that the desired cost reduction would be difficult to obtain, and this work was accordingly discontinued.

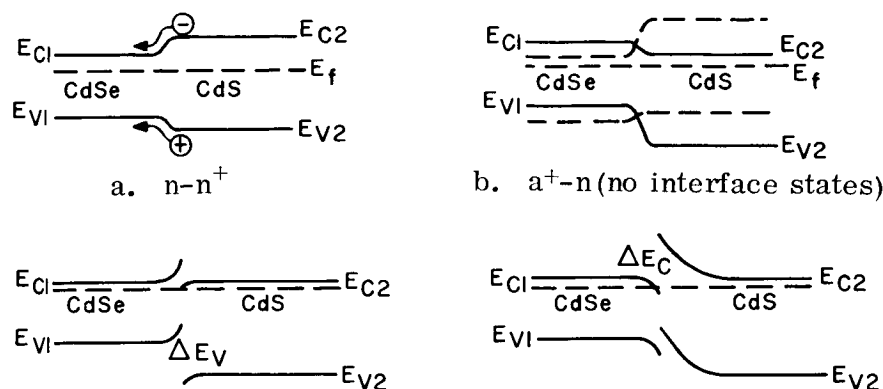
A somewhat similar approach to making silicon thin-film cells was taken by a group working at GE laboratories during 1960-1961 (443). Silicon layers were deposited by the hydrogen reduction of silicon tetrachloride, but layers suitable for cell fabrication were not obtained, and the group subsequently turned its energies to the cadmium telluride thin-film cell work, described above.

More recently, during the period 1964-65, work aimed at fabricating thin-film silicon cells was performed at Ion Physics Corporation with USAF support (295, 296). Silicon films were deposited onto a variety of metallic (tungsten, tantalum, molybdenum, nickel) and non-metallic (silica, silicon, mica) substrates, by rf plasma deposition.

Difficulty was encountered in obtaining adequate adhesion to the substrates, especially when films with large crystallite sizes were formed. In addition, the mobilities and minority carrier lifetimes were found to be much smaller than in single-crystal material. However, it was felt that some films were obtained with properties adequate to allow cell formation, and junctions were made by normal diffusion, by growing successive n- and p-type layers during deposition, by alloying, and by ion implantation. Very leaky diodes were obtained with all of these processes, and even when the cells were diced into diodes with areas of 15 x 15 mils, the photovoltaic conversion efficiencies of these were found to be only around 0.01%. Although it was felt that the various technological problems could eventually be solved, the work on ion-implanted dendritic cells offered the possibility of achieving the same low cost, light weight, and large area objectives more rapidly, and the thin-film cell investigation was discontinued in 1965.

Some interest has been taken by various groups in CdSe cells and related devices. Vishchakas of the USSR reported on the properties of vacuum deposited CdSe layers in 1957 (470), giving details of electrical conductivity, photoconductivity, and optical properties, including their dependence on specimen preparation and heat treatment. Photovoltaic properties were not reported, but in 1965 Kandilarov and Andreytchin of the Bulgarian Institute of Physics published such data (471). These were obtained with specimens made by the sequential deposition of CdS and CdSe on glass, applying gold contacts. The best results were obtained with both the CdS and CdSe layers about 3 μ m thick. Both layers always had n-type conductivity. The possible band structures for n-n⁺ and n⁺-n heterojunctions are as shown in Figure 83 a and b, and, if interface states exist, as shown in Figure 83 c and d. These imply that if the specimen carrier concentration were to be changed, to give nCdS-n⁺ CdSe, in place of n⁺ CdS-nCdSe, then the photovoltage sign may change. In practice, it was found that the CdS always developed a positive potential under illumination, values up to 300 mV being seen. (This only implies that the changes in carrier concentration which could be obtained experimentally may not have been large enough to produce both types of band structure, and is thus not a refutation of the theory.) Spectral response curves showed peaks around 1.9 eV and 2.4 eV, near the band edges of the CdSe and CdS respectively, as would be expected. Conversion efficiency measurements were not reported, and there was no suggestion that the devices had been made for purposes other than pure research on the electrical properties of heterojunctions.

More extensive work on CdSe thin-film cells was done by Heyerdahl's group at Harshaw Laboratories during 1962 and 1963 (446). CdSe films were deposited by direct evaporation of the compound from a source at about 1000° C, onto glass and molybdenum substrates at about 300° C. (The variation of substrate temperature in the range 250-450° C was found to make little difference to the quality of the resulting film). Cells were made by the analog of the dip process used for CdS cells, by immersion of the cells for about 1 sec. in CuCl aqueous solution with a pH about 3 to 4, followed by washing, and a heat treatment in air at 140° C for 50 minutes. This formed a layer of Cu₃Te₂ a few thousand Å thick, and a vacuum-evaporated gold grid was used to



c and d. Interface states present giving dipole layers with different polarities.

Figure 83. Band structures at CdSe-CdS heterojunctions.
(After Kandilarov and Andreytchin)

make contact to this layer. Electrical measurements as a function of temperature, and spectral response data, showed features similar to those obtained with CdS cells, indicating that the CdSe and CdS cells had some extrinsic response mechanism in common. However, the extrinsic response in the CdSe cells was not as pronounced, leading to lower efficiencies ($\sim 1\%$) than in the CdS cells. Consequently, the work was not pursued further.

The French group at the Laboratoire d'Héliotechnique investigated a number of possible thin-film solar cell materials, including GaAs as described above in IV-D-4 (466). Alloys of $Ga_{1-x}In_xAs$ and $Cd_{1-x}Hg_xTe$ were used, films being formed by the three-temperature technique with coevaporation of the alloy components under vacuum. Optical absorption measurements indicated that the bandgap varied with the alloy composition, as expected. With the $Cd_{1-x}Hg_xTe$ films, n- and p-type conductivity could be obtained at will by varying the substrate temperature during film growth. Cells made in this way showed photovoltages, but the values were small (~ 10 mV), and the cell efficiencies seen were also low, high series resistance being a further contributor to this.

Bate and Taylor reported a method for obtaining thin layers of indium antimonide, InSb, in 1960 (472). This consisted of squashing a drop of the molten compound between two glass optical flats. The resulting thin layers were of course polycrystalline, but showed electrical and optical properties not much changed from those of single-crystal material. However, the energy gap of InSb is too low for this material ever to find application in solar cells.

This completes the historical review of thin-film solar cells. Major attention has been focused on those devices most likely to provide good conversion efficiency, but all other cells have been covered so far as they have been reported in the literature. Information on certain other more specialized types of thin-film devices will also be found in sections IV-E and IV-F, dealing with the high-voltage photoeffect and organic materials, respectively.

E. HIGH-VOLTAGE PHOTOVOLTAIC EFFECT

The first recognition of the high-voltage photovoltaic effect, and systematic analysis of the effect, was made by the group working under a U. S. Army Signal Corps contract (152) at RCA Laboratories, in the period November 1956 to February 1957. The effects were seen in CdTe thin films deposited on glass substrates, with the evaporant stream during deposition striking the substrate obliquely rather than at the usual normal incidence. Voltages of up to 320 V were developed under illumination, between conducting contacts on the substrate ('TIC coating') ~ 2 in. apart. The conclusions reached on this effect were:

- a. The oblique deposition of CdTe, ZnS and CdSe produced films showing the effect.
- b. The photovoltages varied as the logarithm of the illumination intensity.
- c. The photovoltage changed rapidly with temperature, decreasing with increasing temperature.
- d. The specimen resistance was high (10^9 Ohms/ \square or higher), and the characteristic appeared ohmic.
- e. The entire specimen contributed to the effect, the voltage not being developed at isolated regions.

Bearing in mind these observations, it was proposed that the specimen structure was as shown in Figure 84 (a), with the band structure shown in Figure 84 (b). The voltage was developed by serial addition of small photovoltages arising at the grain boundaries.

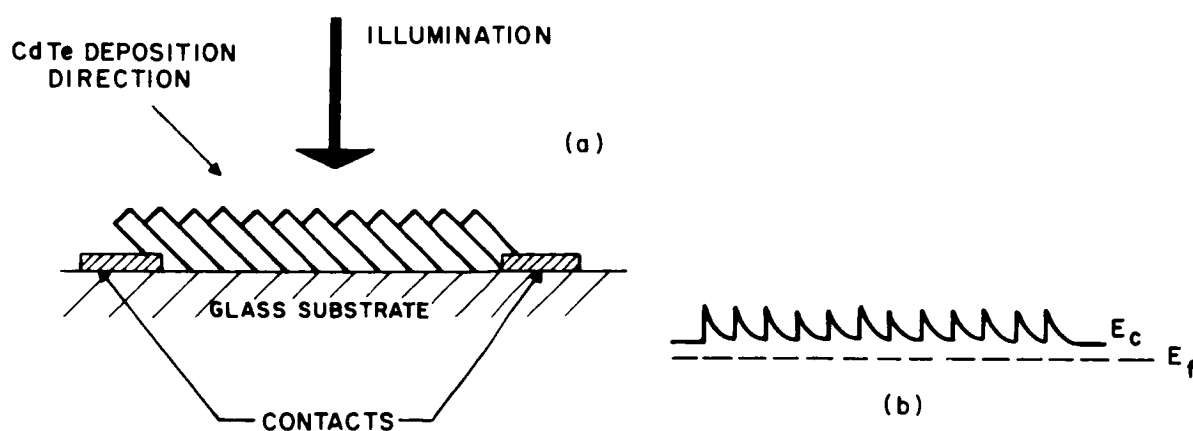


Figure 84. (a) Disposition of crystallites in a CdTe film showing the high-voltage photoeffect, after Pensak. (b) Band structure of a CdTe film showing the high-voltage photoeffect, after Pensak

The results reported exhibited another characteristic seen by all subsequent workers in this field: the voltages measured were highly variable, and could even be reversed in direction by heat treatment of the specimen. Although they did not observe photovoltages in PbS, it was recognized by this group that the observation of photovoltages up to 2 or 3 V in PbS films by Starkiewicz, Sosnowski, and Simpson (147) implied that these workers had seen the effect without realizing fully the significance of a photovoltage greater than bandgap. The RCA group proposed the use of the effect for photovoltaic power generation, although the high resistance of the cells was noted as being a possible problem area. It appears that the work which has been done in succeeding years has added to the range of materials known to exhibit the effect, has elucidated the underlying mechanism to some degree, but has done virtually nothing to bring the application of the effect any closer.

Apparently independently of the RCA Laboratories work, a Russian group reported the observation of larger-than-bandgap photovoltages in PbS films deposited under vacuum at an oblique angle (473). This report showed a photomicrograph of a cross section of one of the specimens used, demonstrating a markedly dendritic surface texture. These workers also found a strong dependence of photo-emf on illumination angle, results showing that the photovoltage could be made to change sign by illuminating the specimen through the glass substrate rather than on the exposed surface. Again, heat treatment was found to strongly influence the behavior of the specimen.

Following the initial work done at RCA Laboratories, continuing interest and progress was shown by those associated with this group, resulting in a series of publications during 1958. Pensak (474) published the results noted above for CdTe as did Goldstein (475), and these workers reported more fully on their results in 1959 (476) while Merz (477) and Ellis et al. (478) reported on effects seen in single-crystal wafers of ZnS. The latter reports take particular concern of the mechanism underlying the effect. Crystallographic studies of the vapor-grown ZnS platelets used as specimens showed that the (111) crystallographic direction always lay parallel to the plane of the platelet, and that the surface exhibited a set of microscopic parallel striae. It appeared that these striae were demarcation lines between regions of cubic and hexagonal material, and Merz pointed out that this growth pattern could be obtained by a rotation of the crystalline axes by 60° in the same direction about the (111) or (0001) axis at each interface. Because the direction of rotation was the same at each boundary, a net polarization or directionality could be introduced into the structure by this growth habit, leading to the additive effects seen for the photovoltages. By counting striae and measuring the volts-per-centimeter developed by these specimens, these workers concluded that each junction contributed about 0.15 V to the output. Merz showed that this would be consistent with the band picture for the structure, which was essentially the same as that shown in Figure 84 (b).

In 1958 and 1959, work on ZnS single-crystal specimens in which photovoltages up to 20 were seen, was reported by Cheroff, Keller, and Erick (479, 480) working at IBM Laboratories. The results were similar to those of the RCA group, but in addition spectral response measurements were performed which showed that the sign of the photovoltage was dependent on wavelength of illumination. This result had been reported earlier in

1959 by Lempicki (481,482), who also confirmed that the larger-than-bandgap photovoltages appeared only along the (111) direction, and also appeared only in crystals containing stacking faults, in agreement with the work of Merz and Ellis et al. The wavelength dependence of photovoltage was found to show a sharp positive maximum near 3400 Å, with smaller negative values for both longer and shorter illumination wavelengths.

An explanation of the observed effects was offered by Tauc in 1959, which accounted satisfactorily for the phenomena (483). Tauc proposed the existence of two junction types, which could arise from a combination of the difference in E_g values for cubic and hexagonal material, together with systematic changes in impurity concentration. The resulting band diagram is shown in Figure 85. Under high intensity illumination with photon energy $E_{g\text{ cub.}}$, a photovoltage ΔE per structural unit is produced. On increasing the photon energy, a photovoltage caused by the barriers in the stacking faults appears, which has a value

$$V = \frac{\Delta E_2}{q} = \frac{(E_{g\text{ hex}} - E_{g\text{ cub}})}{q} - \frac{\Delta E_1}{q} \quad (129)$$

Since ΔE_1 and ΔE_2 are in opposite directions, the overall photovoltage changes sign. On further increase of photon energy to $E_{g\text{ hex}}$, the gradient in the hexagonal material produces a photovoltage ΔE_3 , and the overall photovoltage decreases to zero:

$$-\Delta E_1 + \Delta E_2 - \Delta E_3 = 0 \quad (130)$$

With further increase of photon energy, the ΔE_2 contribution decreases so that the overall photovoltage becomes negative, and the experimentally observed dependence of photovoltage on wavelength is obtained.

An alternative hypothesis was advanced by Hutson (484) in 1961, who was associated with Cheroff in the IBM Laboratories group which investigated the high-photovoltage effect. Hutson pointed out that the nature of the barriers assumed to exist in the specimens showing the effect by Pensak, Merz, and others was not clear. Hutson proposed that the barriers arose by the piezoelectric effect caused by strain gradients occurring at stacking faults and grain boundaries. The gradients were assumed to arise because of the difference in thermal expansion coefficient between cubic and hexagonal ZnS, the strain arising from differential expansion between ZnS and substrate. Clearly, this hypothesis did not cover the case when free platelets of ZnS were used for specimens, as in the work of Merz.

Further measurements on the dependence of the photovoltage on illumination wavelength for ZnS, over the temperature range 77 to 580°K, were reported by Cheroff (485) in 1961. Whereas the photocurrent increased uniformly with increase of temperature, the photovoltage was found to reach a minimum at 430°K, and to increase with increasing temperature above this point. Hence, Cheroff felt that a simple p-n junction theory could not fit the observed facts, and an explanation of the type proposed by Hutson was presumably felt to be more likely.

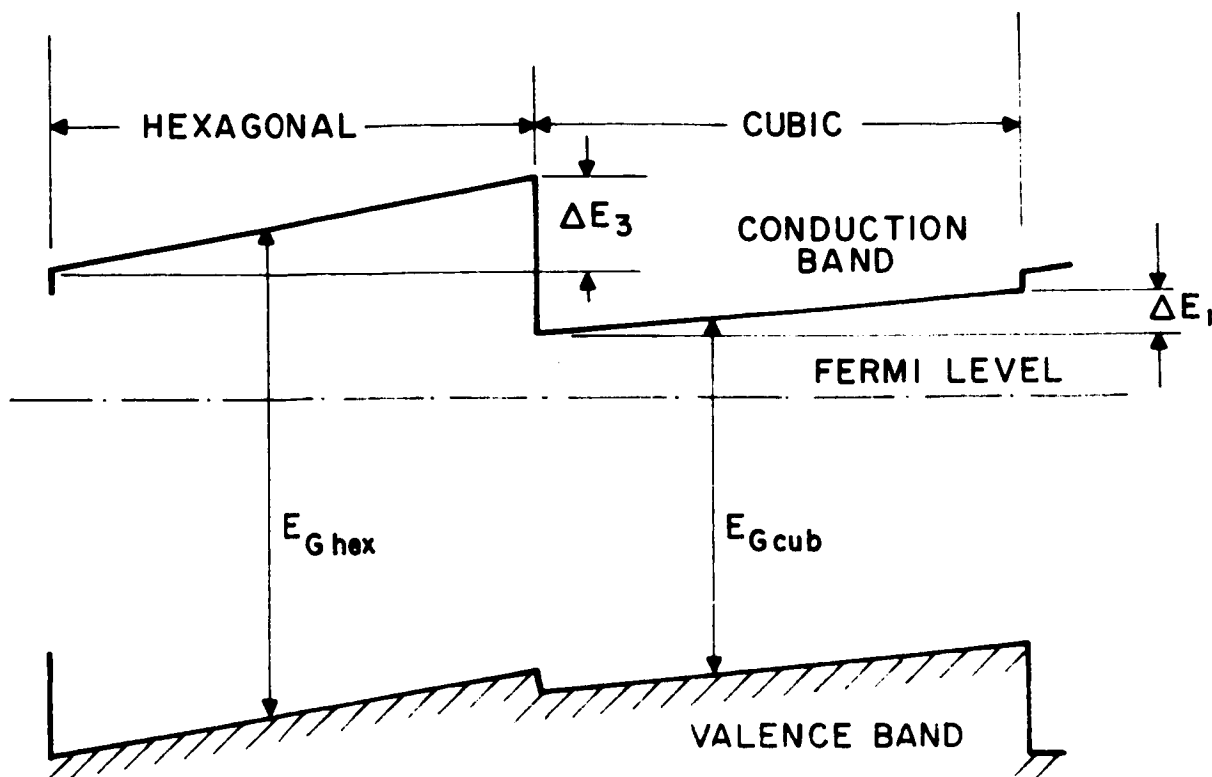


Figure 85. Band structure leading to the high-voltage photoeffect, after Tauc

The range of materials known to exhibit the high-voltage photovoltaic effect was considerably extended by the work of Lyubin and Fedorova in 1960 (486) and 1962 (487). Work with CdTe layers was reported, the spectral dependence of photovoltage being measured, and a photovoltage sign reversal at about $5,500 \text{ \AA}$ being seen. In addition, high photo-emf's were seen in Sb_2Se_3 , Sb_2S_3 , $\text{Sb}_2\text{S}_3\text{-Sb}_2\text{Se}_3$, $\text{Sb}_2\text{S}_3\text{-Bi}_2\text{S}_3$, and $2\text{Sb}_2\text{S}_3\text{-Bi}_2\text{S}_3$, and photo-emf sign reversals were reported as occurring in some of these samples with change of illumination wavelength and direction, as for CdTe. Lyubin and Fedorova found no consistent correlation between deposition angle and photovoltage direction, observing photo-emf's up to $80 \text{ V}\cdot\text{cm}^{-1}$ for films deposited at normal incidence. They thus rejected the hypothesis of Pensak, Goldstein et al., proposing initially that the underlying anisotropy arose from photocurrents existing during film formation, although it is not clear how such photocurrents could arise before the anisotropy was present. The later report (487) favors the mechanism of Semiletov for the photo-emf formation.

From 1962 onwards, the bulk of both the experimental and theoretical work has been done by Soviet workers from several laboratories, interest in the U.S. apparently having waned because the high specimen resistance, and lack of uniformity of results indicated that the application of the effect to power generation would not be possible.

Semiletov (488) reported the results of electron-diffraction measurements on CdTe vacuum-deposited thin films, which established that although crystalline CdTe normally exists with the cubic zincblende structure, in thin films a hexagonal wurtzite structure can also be stable. Semiletov's earlier work had also shown that in CdTe films containing both phases, the transitions between the two stacking patterns were not random, but occurred with a certain regularity. This was analogous to the system proposed by Merz to explain the high-voltage effect in ZnS. Semiletov established that in CdTe films showing high photovoltages:

- (i) The crystalline orientation was strongly influenced by the deposition direction, the (111) or (0001) axes being parallel to the direction of the impinging evaporant.
- (ii) Two phases were present (cubic and hexagonal).
- (iii) A large number of stacking faults existed in the hexagonal phase.

Observation (i), coupled with the hypothesis that the photovoltage was always developed along the polar (111) or (0001) axis (as had been established by Merz for ZnS), showed why oblique deposition is necessary for CdTe high-photovoltage specimens, since deposition normal to the substrate would result in crystallites having the (111) or (0001) direction perpendicular to the substrate. Semiletov's results therefore tend to support Merz's explanation for the effect. Novik and coworkers in a series of publications during 1962 and 1963 described experiments performed on CdTe layers formed by vacuum deposition onto cleaved surfaces of NaCl, KCl, and KBr (489-491). The substrate was found to have an orienting effect on the grown film, but the CdTe was found to form the alternating cubic-hexagonal growth pattern characterized by Semiletov, and this result thus supported Merz's work.

The later publication by Novik (491) reported that the application of an electric field of $10\text{--}12\text{ kV}\cdot\text{cm}^{-1}$ normal to the substrate surface during deposition caused a marked drop and in some cases a reversal in the photo-emf direction for one field polarity, but a negligible effect on photo-emf for the opposite field polarity. Novik's report of a photovoltage of $1\text{ kV}\cdot\text{cm}^{-1}$ for CdTe films grown on KBr appears to be the largest field strength seen to date.

Neumark, working at Philips Laboratories (New York), proposed a theory of high photovoltage production (492) based on the work of Tauc and Hutson but differing from these theories in important respects. Feeling that the fields due to nonuniform donor concentrations in the hexagonal and cubic regions, as proposed by Tauc, were unlikely, Neumark proposed that the necessary fields arose from spontaneous polarization of hexagonal ZnS. The resultant band structure is as shown in Figure 86, and the mechanism of photovoltage production and its dependence on illumination wavelength follow the analysis of Tauc, described above.

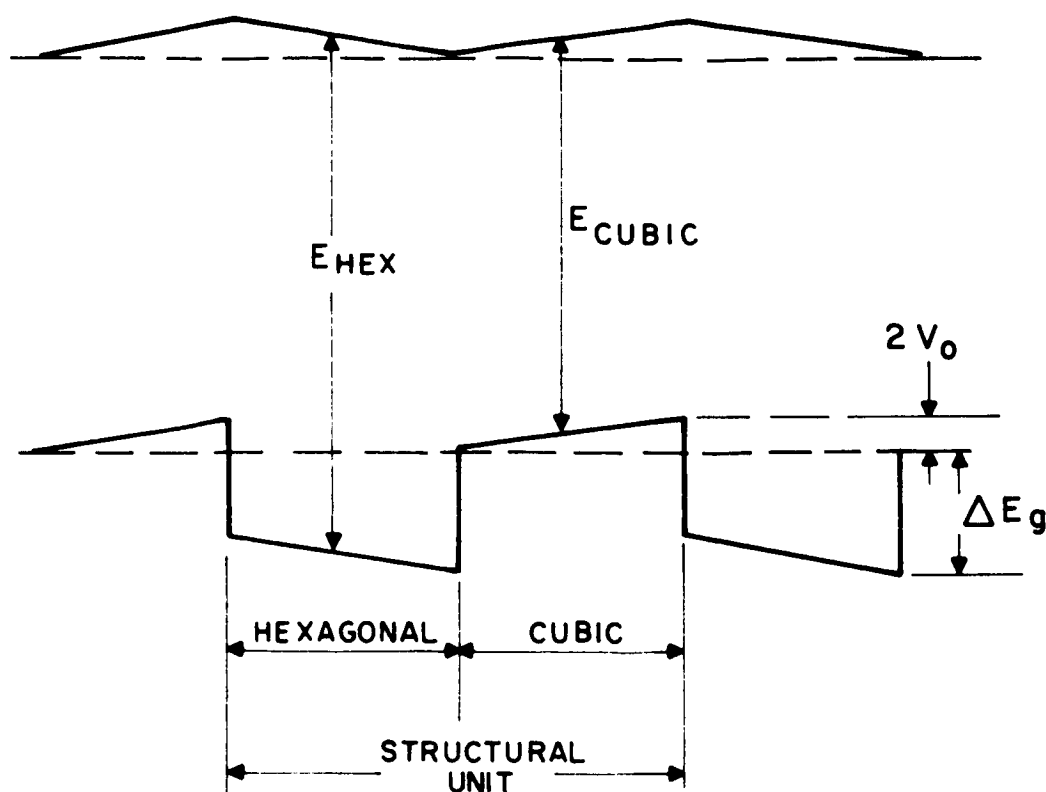


Figure 86. Band structure leading to the high-voltage photoeffect, after Neumark

In 1963, Karpovich and Shilova (493) described work amplifying the results of Lyubin and Fedorova on thin films of Sb_2S_3 . It was found that residual oxygen was necessary during deposition to obtain photovoltaic films, and the usual oblique deposition process was used. The results were given for experiments in which photovoltage was measured as a function of deposition angle, illumination angle, light intensity, and wavelength, over the temperature range 90 to 350°K. A photovoltage sign reversal with illumination angle and wavelength was seen for some specimens. An explanation in terms of competing p-n junctions of different "qualities" at the grain boundaries was offered.

In 1964, Brandhorst and Potter (494) reported the observation of photovoltages larger than the bandgap in silicon and SiC films grown under vacuum on MgO and SiO_2 substrates. The specimen resistances were in the 10^{10} -Ohm·cm range, and voltages of up to 5.2 V were observed. On removal of the illumination, the photovoltages were observed to decay at a rate corresponding to a time constant of some tens of seconds. This suggested that trapping effects were the cause of the photovoltage, and Brandhorst and Potter proposed an explanation for the effect based on space charge produced by a nonuniform distribution of trapping centers.

In 1964 appeared the first of a continuing series of publications by Adirovich and his co-workers. These reported specimen preparation methods and experimental results obtained with silicon films (495-497) and GaAs films (498) prepared by vacuum evaporation. Spectral response and photovoltage dependence on illumination angle were investigated, with results not significantly different from those reported for CdTe, described above. In (499) and (500), possible mechanisms for the high-voltage photoeffect were discussed. The conclusion was reached that the Dember effect was the cause of the photovoltage in Ge, Si, and GaAs films, but that in CdTe the multiple p-n junction effect was present. This was mainly based on the evidence that in Ge, Si, and GaAs films, a photovoltage sign reversal was observed on rotating the direction of illumination relative to the specimen plane by 180° , whereas for the CdTe films this effect was not seen. This observation runs contrary to the results of Lyubin and Fedorova (486), but these results appear to be at variance with those of most other workers, so that this is perhaps caused by experimental difficulties rather than having a more fundamental significance. More recently, Adirovich has considered transient effects in CdTe photovoltages (501), obtaining results consistent with the cells operating with a series array of p-n junctions. Adirovich's conclusion that the high photovoltages seen in silicon films were due to the Dember effect runs contrary to the hypothesis of Brandhorst and Potter, described above, and Adirovich points out that there is reason to doubt the validity of the analysis of these authors.

In 1966, Perrot, David, and Martinuzzi (466) also reported the observation of high photovoltages in GaAs films prepared by a method superior to that employed by Adirovich, eliminating any suspicion that the sample preparation technique used by the latter may have led to specimen inhomogeneities which would invalidate the results.

Korsunskii and Fridman (502) reported capacitance measurements on CdTe films exhibiting the high-voltage photoeffect, which support the multiple p-n junction hypothesis of operation. Palatnik and Sorokin (503) have reported an investigation of the effect of the substrate material on the photovoltages seen in CdTe films, showing that films on single-crystal sapphire produced markedly higher photo-emf's than those formed on glass. The effect of substrate temperature during film growth on the magnitude of the photo-emf was found to lead to lower voltage values with increasing crystallite size, again supporting the multiple-p-n-junction hypothesis.

Recently, Ignatyuk and Novik (504) have reported the observation of high photovoltages (up to $800 \text{ V} \cdot \text{cm}^{-1}$) in films of ZnTe vacuum-deposited onto cleaved NaCl, KCl, and KBr crystals, thus adding another material to those known to exhibit the photovoltages larger than bandgap.

This, then, is the present situation regarding the high-voltage photoeffect. It is seen that the initial results, so promising for application to power-generation systems, have been amplified by the subsequent work, but no solution to the problem of high device

impedance has been found. The explanations offered for the phenomena fit the facts better now than during the early work, but there seems to be little doubt that the last word has not been spoken on this topic, since the wide range of experimental results defy simple explanations. In any case, the present situation indicates that there is no possibility of employing high-photovoltage devices as energy converters in the near future.

F. PHOTOEFFECTS IN ORGANIC MATERIALS

Organic compounds exhibit three types of photoelectric behavior:

- a. photoconductivity
- b. sensitization of photoeffects in other materials
- c. photovoltaic action

Of these effects, the first is of no direct significance for the purposes of the present work, whereas the other two may have applications in the future. Although photoelectric effects in organic compounds were first studied during the 19th century, it is only recently that an appreciable research effort has been applied to the field. For this reason, the whole topic of electrical activity in organic materials is not as familiar as the analogous activity in inorganic materials. The first part of this section attempts to provide some background information on electrical conduction in organic materials, and the two later parts will describe sensitization and photovoltaic effects. U. S. government research contracts in this area are summarized in Table XXI, Appendix III.

1. Electrical Conduction in Organic Solids

The material presented here has largely been drawn from Gutmann and Lyons' recent book on organic semiconductors (505), to which the reader is referred if more detail is needed. This is a relatively young field of research (the above reference is the first book devoted entirely to the subject), and there still exists considerable controversy over some of the basic issues; where two theories are extant, both have been mentioned.

In elemental inorganic semiconductors, the bonds which hold the atoms in the crystalline lattice are of the same strength as those which bind neighboring atoms together; this remains very nearly true in the inorganic compound semiconductors. Hence, there is a strong interaction between the allowed energy levels for electrons of the component atoms, and a well-developed band structure is present as a consequence. However, in organic solids, the bonds between atoms which make up each molecule of the compound are, in general, much stronger than the bonds between molecules which form the crystal

lattice. There is strong coupling between the electron energy levels within the molecule, but a weak coupling between electron energy levels in adjacent molecules. A continuous band structure throughout the solid does not arise, and the resulting discontinuities in band structure between adjacent molecules can provide a major barrier to electrical conduction. Thus, electrical conduction occurs by the production of a free electron or hole by a transition between energy levels inside the molecule, followed by the motion of the free carrier past the intermolecular barrier. It is the effect of this second process which sets organic conduction processes apart from their inorganic analogs.

Two mechanisms have been proposed for the motion of the free carriers past the intermolecular barriers. One postulates that the barriers are sufficiently narrow to allow electrons to tunnel through them, the second says that the barriers are of such dimensions that electrons must pass over the top and "hop" from molecule to molecule.

When an organic photoconductor is illuminated, it is believed that (in most cases) an electron is excited from a lower to a higher energy state within the molecule. Conduction will now be governed by the rate at which electrons can pass through the intermolecular barriers. If tunnelling processes occur, therefore, the photocurrent should be relatively insensitive to temperature, whereas if hopping processes occur, an exponential dependence of photoconductivity on temperature should be seen, with the exponential constant a measure of the barrier height. In practice, both types of behavior have been seen, and it seems reasonable to suppose that both processes can, in fact, occur.

Now the processes discussed above reasonably lead to electrical conductivity values of $10^{-4}(\text{Ohm}\cdot\text{cm})^{-1}$ or smaller. Some organic materials exhibit conductivities of $1.0(\text{Ohm}\cdot\text{cm})^{-1}$ or higher, however, and this observation reaches its limit with graphite, which has a conductivity of $10^4(\text{Ohm}\cdot\text{cm})^{-1}$, approaching the metallic. It is necessary to consider how this may occur.

It is believed that the conduction electrons in an organic solid come from the π orbital in aromatic compounds. This π orbital is a unique feature of the benzene ring; a representation of the orbital is shown in Figure 87. It appears as a pair of donut-shaped regions above and below the plane of the benzene ring, and in these regions the 18 electrons forming the ring bonds are most likely to be found. From the point of view of electron energy, the orbital is a single entity, and no barrier to electron motion between the two regions of the orbital exists. In solids with a crystal structure such that π orbitals from adjacent molecules can overlap appreciably, easy electron transfer between molecules can occur. Normally, this mainly happens when the planes of benzene rings are linked to form sheets, as in the extreme case in graphite. This mechanism also implies that electrical conduction parallel to the plane of the rings will be easier than conduction perpendicular to the plane of the rings, as is observed. This same phenomenon appears to occur in the TEA salt of TCNQ,²¹ where stacked columns of benzene rings parallel to each other occur (see Figure 88). The conductivity of this salt is about $1.0(\text{Ohm}\cdot\text{cm})^{-1}$ and is a maximum parallel to the stacking direction.

²¹TEA = triethylamine

TCNQ = tetracyanoquinodimethane

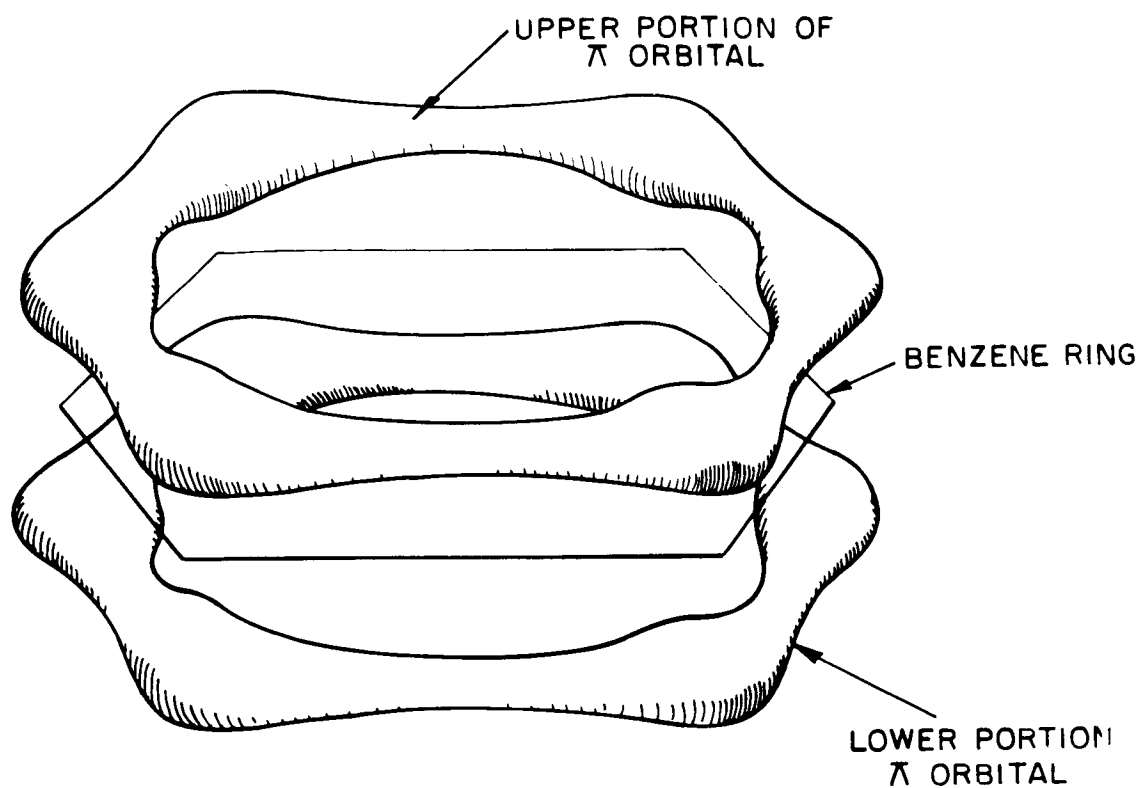


Figure 87. Representation of the π orbital for a benzene ring

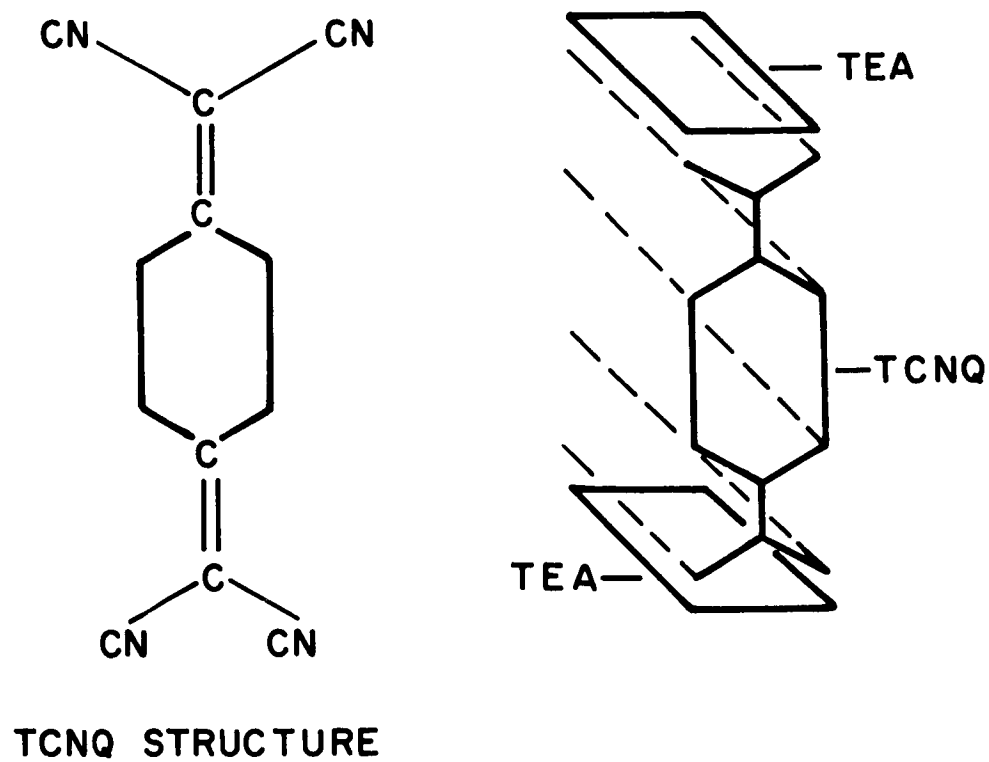
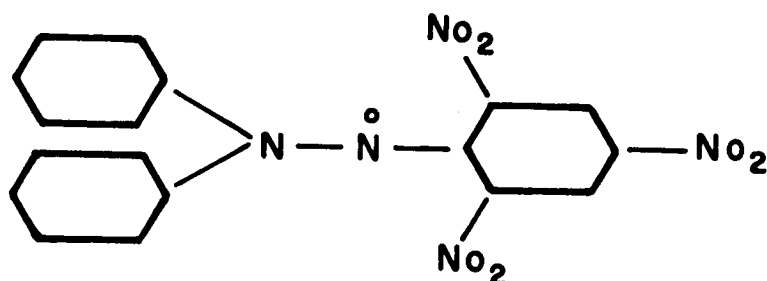


Figure 88. The structure of TEA salt of TCNQ

Another group of organic compounds with large conductivities are the "free-radical" solids, in which an unbonded valence electron occurs. An example is DPPH,²² with the structure shown in Figure 89. The unpaired electron is free to move in the molecule without any transition to a higher energy state, and this may explain the high conductivity of this and similar free-radical solids.

A third group of high-conductivity solids is comprised of the charge-transfer complexes. In these, two molecular species are present, one an electron donor type and the other an electron acceptor type, although in some compounds, different regions of one molecule may exhibit the necessary donor and acceptor characteristics. Because of the partially ionic character of the intermolecular bonding in these solids, the interaction can be strong enough to cause appreciable band formation, thus raising the conductivity.

Another class of compounds also has high conductivity for a related reason. These are the polymers, in which bonding between constituent molecules occurs by the polymerization process, leading to strong intermolecular bonding and interaction. This process could, in principle, proceed to the point where a crystal lattice formed of strong covalent bonds would be produced, as in the inorganic semiconductors. In fact, few polymers show high conductivities, but the above explanation may account for the results with poly-copper-phthalocyanine, which after heat treatment can have a conductivity of $0.25 \text{ (Ohm} \cdot \text{cm)}^{-1}$. Similarly, the TCNE²³ polymeric chelates have high conductivities [$20 \text{ (Ohm} \cdot \text{cm)}^{-1}$], but these are also charge-transfer complexes. Graphite would also, in principle, fall into the category of polymers, and this would help to account for the high conductivity.



α, α' -DIPHENYL- β -PICRYLHYDRAZYLE (DPPH)

Figure 89. The structure of DPPH

²²DPPH = diphenyl- β -picrylhydrazyle

²³TCNE = tetracyanoethylene

This account has stressed the mechanisms underlying those compounds which exhibit high conductivity because the major difficulty with organic photovoltaic devices fabricated up to the present has been their high internal impedance.

However, use as photovoltaic semiconductors is only one of two possible uses for organics. Dyes may also prove useful as sensitizing materials, used in conjunction with inorganic semiconductors. Dyes, in general, exhibit photoconductivity, but have resistivities much too high to make them interesting as semiconductors. It should be noted that although the photoconductive and photovoltaic spectral response of many organic materials follows the optical absorption curve, this is not always true, since organic molecules are sufficiently complex to allow a large number of photon absorption mechanisms other than straightforward electron transitions. This is in contrast to inorganic semiconductors, where optical absorption normally takes place by breaking bonds in the crystal lattice to form electron-hole pairs.

2. Sensitization

The fact that certain organic materials can act as sensitizers in silver halide photography was first observed during the 19th century (506, 507). The sensitizing material is applied as a thin film to the emulsion side of the plate or film, and increases the long-wavelength (red) response. The mechanism of the effect is now understood (508); the fundamental photographic process relies on photoconductivity in silver iodide, and the sensitizer acts by absorbing low-energy photons and transferring the energy to the AgI_2 either as a free electron or as an exciton which reacts with the AgI_2 to create a free electron. This effect, although understood only recently, was the first application of the photoelectric sensitivity of organic materials.

The sensitization of photoconductivity in silver halides, CdS , and other semiconductors has been much studied recently, and a wide variety of organic compounds have been found to be capable of displaying the phenomenon. There has been, and still is, considerable debate over the mechanism of energy transfer between the sensitizer and the base material. This is partly due to direct contradictions in the experimental evidence obtained by different groups, probably resulting from differences in the sample preparation techniques. The situation in this respect appears to resemble that existing during the early work on semiconduction, before the means for growing single crystals of semiconductor grade purity were available. As Gutmann and Lyons point out, it is not at present possible to prepare organic compounds free of other organic contaminants with the degree of purity possible with inorganic compounds or elements. For this reason, the whole subject of organic semiconduction is in a state of flux, since only a few of the experimental results are firmly established, and the interpretations of the effects seen vary widely.

Nelson has reported an extended series of experiments aimed at investigating photoconductivity sensitization (509-514). The semiconductor used was CdS , and the photoconductive response to light in the wavelength range 6000 to 9000 Å was found to be

increased by pinacyanole, kryptocyanine, and neocyanine (509). It was also observed that with some experimental cells, photovoltages were generated, as discussed in the next section of this report. Similar sensitization effects for chlorophyll a and methyl chlorophyllide a were also seen by Nelson (510).

Later work by Nelson was aimed at elucidating the processes occurring during sensitization. When a dye molecule on a CdS surface is excited by the absorption of a photon, four possible events may follow:

- a. The energy is transferred directly from the dye to the CdS without the formation of a free charge carrier (exciton transfer, or resonance transfer).
- b. A free carrier is formed, which passes into the CdS.
- c. A photon is re-emitted from the dye, or
- d. the energy is degraded by phonon production in the dye molecule.

In the sensitization process, a. or b. is apparently dominant over c. or d., and hence the mechanism debate centers on whether a. or b. is the process giving rise to sensitization. Nelson proposes that the photovoltaic effects seen between dye and CdS demonstrate that electron transfer between dye and substrate occurs, and hence that this is the mechanism of sensitization. As Nelson points out, the evidence is not conclusive, but this model fits the observed facts better than the alternatives.

A great deal of work has been done by the Russian group working under Terenin, on sensitization effects. Experiments by Putseiko (515) were performed using ZnO, and the measurements made were of photoconductivity (measured directly), and the production of a photo-emf at the surface of the ZnO, (using the "Bergmann condenser" method.) The results indicated that many dyes acted as sensitizing agents, and that the conductivity type of these dyes could be either p- or n-type. This was taken to indicate that the fundamental process occurring during sensitization involved the transfer of energy directly from dye to semiconductor, the energy then creating free carriers in the inorganic semiconductor. In this way, the sense of the photovoltage would depend only on the nature of the inorganic semiconductor, as was observed. Putseiko also found that the spectral sensitivity of the sensitization effect followed that of optical absorption in the dye, and that the thinnest dye layers (down to one monolayer of molecules) produced the largest effects. However, some sensitization could be obtained by pressing a disc of dye against the semiconductor surface, without the necessity for producing the more usual intimate dye-substrate contact by deposition of dye from a solvent.

Thus, there appears to exist the possibility that the long-wavelength sensitivity of inorganic semiconductor photovoltaic cells may be increased by the application of the sensitization effects described above. The compound semiconductor cells, and probably the CdS cells particularly, are the most likely to make use of the phenomenon. It appears

that a comprehensive experimental program is the only way of approaching this question, and such a program has not yet been run. It is also clear that the practical application of this effect in cells for space use would require that the sensitizing material be stable under UV and particle irradiation. This is a problem area for organic materials, and will be more fully discussed in the evaluation sections of this work.

3. Photovoltaic Effects

Photovoltages have been seen at electrolyte-organic, metal-organic, and organic-organic interfaces, though the latter is unusual.

Electrolyte-organic photovoltages were reported by Kallman and Pope (516) in 1959, using NaCl solutions and anthracene crystals. The maximum photovoltage observed was 0.2 V, under unstated illumination conditions, with a low power conversion efficiency because of the high internal impedance of the cell. For obvious reasons, such Becquerel cells are of no practical interest for power conversion systems for space use, and the significance of such work is for research purposes only.

Photovoltages ranging from millivolts to some hundreds of volts have been reported for metal-organic contacts; Gutmann and Lyons (505) provide a useful summary of the data from many authors. In most cases, uncertainty exists concerning the origin of these voltages, some authors concluding they are due to Dember effects, others to contact effects. In some instances, particularly for the 230 V observed when polyethylene was irradiated with UV (517), the effects may be due to charge release, as noted by Gutmann and Lyons. The photovoltaic work can best be summarized as follows:

The majority of the specimens have been made in the "sandwich-cell" configuration of Figure 90(a), though some use has been made of the "surface-cell" geometry of Figure 90(b). In the sandwich cell, the electrodes are usually metallic, or one may be a conducting coating ('TIC') on the glass substrate; the two electrode materials may or may not be the same. The cell may be illuminated from either side, one electrode usually being made either thin, or given a grid pattern, to provide optical transmission. The surface cell may have both electrodes of the same or of different materials, and either or both electrodes may be illuminated. Many different electrode and organic materials, deposited by various techniques, have been investigated using these cells, and the results are tabulated by Gutmann and Lyons, as noted above. The main conclusions to be drawn from this work are that organic materials exhibit photovoltages analogous to those seen with inorganic semiconductors, but that none of the cells made to date has exhibited a power conversion efficiency comparable to those using inorganic materials.

However, such results as have been obtained have prompted an interest in investigating photovoltages in organic materials for power conversion by the group working under Golubovic at the USAF Cambridge Research Laboratories, and this group has also sponsored a program of research by university and industrial laboratories (518) over the

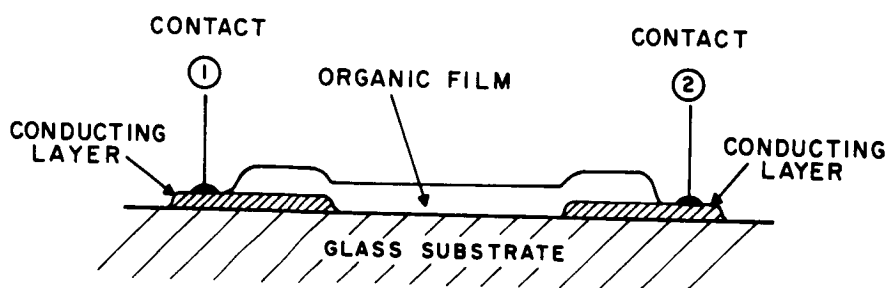
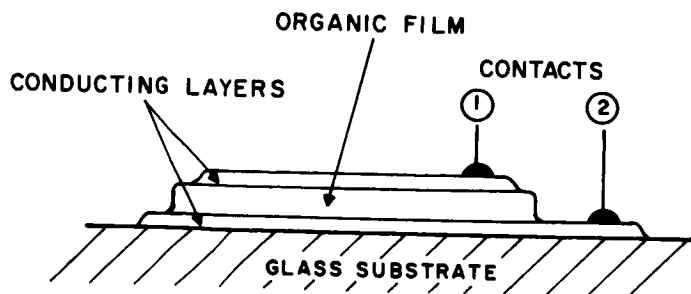


Figure 90. Cells for the investigation of conductivity in organic films

years 1960 to the present. The results of this work have not been widely reported, but recent publications by Golubovic (519)²⁴ and Mukherjee (520) summarize the present status. Golubovic's results have been obtained with sandwich cells with Al and Au electrodes, using either single or double organic layers. Organic materials studied have been tetracene, pentacene, and aceanthraquinoline. It was found that the addition of a second layer of organic material, particularly of the charge-transfer complexes such as TCNQ, TEA-TCNQ, and chloranil, increased both the photovoltage and photocurrent in these cells. Clearly, internal resistance in the cell is the factor limiting the present efficiency. Photovoltages up to 760 mV were seen, with current densities in the $\mu\text{A}\cdot\text{cm}^{-2}$ range for illumination densities of low tens of $\text{mW}\cdot\text{cm}^{-2}$. The spectral response of the cells in general followed that of the optical absorption in the organic material.

Photovoltages possibly arising from p-n junctions between two organic materials have been reported by Meier and Haus (522), and Needler (523). This type of behavior appears to be unusual in organic materials, and metal-organic contacts appear to be more likely to yield useful photovoltaic cells.

²⁴The authors of this report are grateful to Dr. Golubovic for supplying a prepublication copy of this paper.

Photovoltages have also been reported by Nelson, Putseiko, and others as occurring at organic-semiconductor interfaces. Nelson's work (510) was done using a modification of the surface cell, in which one of the electrodes was CdS, with a metal contact to the CdS, while Putseiko's work was done with a sandwich-type cell with one of the electrodes of ZnO. Since most semiconductors (and particularly the compound semiconductors such as ZnO and CdS) exhibit photovoltages caused by an inversion layer at the surface, so that any type of conductor applied to the illuminated surface can be used to form a photovoltaic cell, it appears that the claims that the photovoltage arose in the organic material should be carefully examined, and that the effects seen are possibly due to the usual surface-barrier effects in the inorganic material, modified by the sensitization effects discussed above. Because CdS is always n-type, surface inversion-layer effects will always give rise to a photovoltage of the same sign, which is contrary to the experimental evidence, so that this simple explanation clearly is not always applicable. However, Nelson's band-diagram for the semiconductor-organic contact also suffers from the same difficulty, so that it appears that band-diagram explanations for organic semiconductor effects may be misleading.

This then is the present state of work on organic semiconductors as it pertains to energy conversion. Further evaluation of this work, and a discussion of the future possibilities, will be found in Section V-F below.

V. EVALUATION AND ANALYSIS

GLOSSARY OF SYMBOLS FOR SECTION V

A	empirical constant in the diode equation
E	electric field strength
E_g	forbidden energy gap
E_{ph}	average photon energy above absorption edge
F	fill-factor
I	current
I_L	light-generated current
I_{max}	maximum-power-point current
I_o	reverse saturation current
I_{sc}	short-circuit current
J_o	reverse saturation current density
J_{sc}	short-circuit current density
k	Boltzmann's constant
N_{ph}	density of photo-generated minority carriers
q	electronic charge
R_s	series resistance
T	absolute temperature
V	voltage
V_{max}	maximum-power-point voltage
V_{oc}	open-circuit voltage
η	conversion efficiency
μ	carrier mobility
μ_n	electron mobility
μ_p	hole mobility
τ	carrier lifetime

V. EVALUATION AND ANALYSIS

A. INTRODUCTION

In this chapter, the research and development work on photovoltaic cells which has been reviewed in the previous chapters (II-IV) will be critically examined. Although all of the work of which an account has been given in the previous chapters has been examined in this way, attention will be given in this chapter only to those areas where discussion is felt to be fruitful, or where specific issue is to be taken with reported results. In many cases, of course, criticism and discussion of issues has already been presented in or with respect to publications which have been reviewed in earlier chapters, and these evaluations will not be repeated in this chapter unless there is reason for further discussion. This measure has been taken in order to reduce to a minimum the duplication of material presented in this report. As a consequence, this chapter is complementary to the earlier material, and a balanced picture of the present status of research and development in the solar cell field can only be obtained by combining this chapter with the earlier historical review.

The sequence of the subjects covered in this chapter largely follows that of Chapter IV, so that it has not been necessary in general to refer to the sections where the subject under review has been previously reported: thus, for instance, the evaluation and analysis of theory (Section V-B) is based on the material presented in Section IV-A. When exceptions to this occur, the relevant sections have been indicated appropriately. Similarly, references to publications and reports under discussion have not been given when it is clear from the historical chapters which material is being used. Again, where it is not clear from the earlier chapters, or where new references are used, these have been given as needed.

B. THEORY

In this section, the limitations of the present theories of solar cell operation will be critically examined. Since the acid test of theory is the degree to which it describes a set of facts found in nature, comparisons with experimental data will be used extensively. This should not be taken as a discussion of the ways in which the actual performance of solar cells can be improved in theory, but rather as an examination of the deficiencies in the theory of their operation. Discussion of the means for improving practical cell behavior will be found in the later sections of this chapter.

1. Junction Characteristics

The presently available theories of junction behavior predict I-V characteristics which approximate the experimental results, but do not represent them accurately.

The difficulty arises in the predicted values for I_0 and A in the diode equation:

$$I = I_0 \left(\exp \frac{qV}{AkT} - 1 \right) \quad (131)$$

These are experimentally different from their theoretical values in two respects:

- a. the experimental values of I_0 are many orders of magnitude larger than the predicted values, and the experimental values of A are frequently greater than 2 (and sometimes are 50 or more), whereas the theory cannot account for values larger than 2;
- b. Both A and I_0 are found to be dependent on I : the theory predicts their being constant.

This difficulty has been widely recognized since work with silicon devices became of general interest during the 1950s. It is believed that the theory is inadequate in its treatment of recombination processes, from which the minority carrier lifetimes are calculated. These determine the junction characteristic in the ways shown in sections III-D-2 and IV-A-1. There appear to be two areas of divergence between theory and experiment in the relationship between recombination theory and junction characteristics:

- a. the minority carrier lifetimes predicted from the thermodynamic analysis of Shockley and Queisser (see IV-A-2 above) are many orders of magnitude larger than the experimental values; this arises because in the thermodynamic analysis, only radiative recombination is assumed to occur, whereas in practice non-radiative recombination is the dominant process.
- b. even if the experimental values for minority carrier lifetime are used in the diffusion or space-charge region recombination-generation theories of junction behavior, the theory does not agree with experiment. The reasons for this are not certain, though various hypotheses exist. The work done by Shockley and co-workers, under contract with the USAF, served to eliminate various possible explanations for the anomalous junction behavior, without giving any more plausible explanations which could be analyzed to provide a replacement for the existing theory.

The difficulty at the moment, then, is that experiment indicates that a conduction mechanism is occurring in the cells, either whose nature is completely unknown, or whose behavior has been misinterpreted. A hypothesis which has been advanced by Wolf is that the mechanism is field emission (or tunnel effect) in the rather narrow junctions existing in solar cells. This hypothesis was proposed because of the similarity of form between the solar cell characteristics, and those measured by Chynoweth and

McKay in p-n junctions in which the tunnel effect was known to be dominant. However, Shockley and Queisser pointed out that the solar cell junctions are not as narrow as those of the tunnel effect devices, and one would not expect this to provide an appreciable conduction mechanism in solar cells. They proposed, instead, that metallic impurities in the cells were the cause of the divergence between theory and experiment. Since neither the tunnel effect hypothesis nor the metal-impurities hypothesis has been given adequate quantitative theoretical treatment as yet, their applicability to solar cells cannot be determined.

Although Queisser and Shockley produced experimental results which could be interpreted in terms of metallic impurities being precipitated and "gettered" by suitable heat treatments, the results were not entirely consistent, and were not accepted by these workers as being conclusive proof of the validity of their hypothesis.

Because of its impact on the conversion efficiency of solar cells, this topic is an important one. The elucidation of the processes occurring in the cells, and leading to the presently observed I-V characteristics, could have two possible effects:

- a. The theoretical efficiency calculations could be revised to give a value appropriate to the mechanisms known to occur in the cells.
- b. If the mechanisms which cause the divergence between the present theory and practice were found to be avoidable, the experimental performance of the cells could be improved, to approach more closely the theoretical value calculated from the present theory.

To achieve an advance in the understanding of junction characteristics, it is believed that a combination of experimental and theoretical work would be the best approach, since each could then act as a guide to the other, and the investigation of areas unlikely to give fruitful results can be minimized.

In conclusion, it may be noted that most present theories of junction behavior are built on an assumption of uniformity in the distribution of electrically active species in the planes normal to the current flow. In practice, this is not strictly true, and an approach to explaining junction characteristics by statistical analysis of the effect of non-uniformities in junctions has been undertaken by Shockley and co-workers. This analysis was based on the model of metallic-impurity centers and clusters, which could lead to localized narrow regions giving tunnel conduction or avalanche breakdown. Since the model is multivariable with respect to the nature, size, and spatial distribution of the impurities, the result can be fitted to practically any I-V characteristic, and since experimental correlation on a microscopic scale is not possible, the validity of the theory is difficult to ascertain for a particular device. Further advances in pn junction theory may also be expected in connection with rectifier and transistor development.

2. Ultimate Conversion Efficiencies

The analyses of the type performed by Cummerow, Prince, Loferski, Wolf, and others, based on empirical semiconduction data, provide a valuable yardstick against which actual cell behavior may be measured. Within the limitations of the empirical data on which they are based, and the junction characteristics they assume, such theories must be considered accurate and valid. Although the numerical results obtained by the various analyses which have been published have shown differences, Loferski analyzed these and concluded that these arose from:

- a. differences in the junction theory assumed,
- b. differences in the semiconduction and optical data inserted into the equations, and
- c. differences between the spectral distributions and illumination intensities used.

Basically, the analyses were found to be in agreement, and it appears that further work in this area is not needed at the moment. Should new theories of junction behavior be accepted, this situation would change.

Such analyses are displeasing to the purist because of their need for empirical data on material properties. The thermodynamic derivations of Müser and Shockley are an attempt to found a theory on more basic physical constants. Within the limitations of their assumptions, these theories must also be accepted as valid, though the numerical results obtained by Müser are apparently in error.

The present relationship in this respect, between the thermodynamic junction theories and the phenomenological theories, has been discussed in the previous section.

3. Deviations from Ideal Solar Cell Behavior

Experimental cells depart from the behavior of the ideal cells used in theoretical efficiency calculations in many ways. The effects of various mechanisms which cause these departures from ideal performance have been analyzed, and in general the analysis results are matched accurately by the experimental data.

A major contributor to the difference between real and ideal performance is the diode characteristic: this has already been fully discussed above. The effect is to reduce the V_{oc} value for the experimental cell below that of the ideal.

The ways in which the short-circuit current I_{sc} is reduced below that theoretically possible have been analyzed by consideration of optical reflection and absorption, and of collection efficiency. Judged on the criterion of correspondence between theory and

experiment, these calculations are successful in most respects. The exception is the relationship between reduced cell thickness and collection efficiency, for which most experimental results show a more rapid loss of I_{SC} with reduced cell thickness than is predicted theoretically. This is more fully discussed in section V-C below, and it is felt that the discrepancy is probably caused by extraneous experimental effects which are not accounted for in the theory. Although further work in this area should be performed, it is believed that this would be more fruitfully aimed at eliminating the deleterious effects in the thin cells rather than reworking the theory. The effect of drift fields on collection efficiency also shows a reasonable correlation between theory and experiment, although many experimental results obtained in groundbased and spacecraft radiation damage experiments have shown departures from the theoretical predictions. Again, the basis for these discrepancies is more likely to lie in the experiments than in the theory.

Interestingly, the effect of a direct band-gap on collection efficiency does not appear to have received any attention from solar cell workers. One might expect this to be a relevant point in the operation of GaAs solar cells. An increase in the collection efficiency might be expected because the recombination of minority carriers in a direct band-gap semiconductor causes the generation of photons which can be reabsorbed to create other minority carriers. Thus the minority carrier lifetime in direct band gap semiconductors may not have the same significance for collection efficiency calculations, as it has in indirect band gap semiconductors. In effect, the generation of photons which can re-create minority carriers, adds another mechanism to provide diffusion of carriers in a direct band-gap material. This effect was analyzed by Dumke (523) in reference to devices other than solar cells. Evaluation of Dumke's calculation shows that this is directly applicable to these cells, however, and thus his conclusion can be accepted here also. This showed that the diffusion constant for minority carriers was increased only by a negligible amount by the photon-generation process, and thus this can justifiably be neglected in the theoretical analysis of solar cells made of direct band-gap semiconductors. The different absorption characteristics of direct semiconductors, however, still lead to different design considerations for solar cells made from these materials.

The effect of series resistance (R_S) on cell behavior is to reduce the fill-factor (F) for small values of R_S , with larger R_S values also reducing I_{SC} . In practice, cells with reasonably high efficiencies ($> 6\%$) do not exhibit the latter phenomenon. Many analyses of the effect of R_S on cell performance have been performed, and the theoretical results fit the experimental data well. A related analytical problem concerns the optimization of grid structures, a question considered by Wolf and Lamorte. The shortcomings of their results has already been discussed (see IV-A-3 above). Previous work on the optimization of grid structures is therefore in an unsatisfactory state, and Appendix II of this report contains new results which are believed to be an improvement over those available before. The results of this analysis are in agreement with the conclusions arrived at empirically in cell manufacture, which is taken to demonstrate the validity of the approach taken.

The calculations of Handy to determine R_g allowing for current collection by both grid line and contact strip are not valid, since they are based on erroneous assumptions. The results can be shown to be in error since they indicate that the proportion of current collected by the grid lines will decrease as the grid spacing decreases, which is contrary to the actual case. In fact it can be shown that the effect of current collection directly by the contact strip can be neglected even in 1 x 2 cm silicon cells with 4 mm grid line spacing. In other cells such as the CdS thin-film type, the effect is even smaller. It may be noted that in Handy's paper (224), some confusion between the angles ψ and θ exists. Since the analysis shows θ to decrease with decreasing grid spacing, ψ must increase, and thus the area of the trapezoid which provides current collection onto the grid line decreases, lowering the proportion of current collected by the grid line. This is the opposite of the conclusion stated in Handy's paper.

In general, it is concluded that further detailed analysis of the ways in which solar cell performance deviates from the ideal, is not at present justified, since in all cases the experiments either support the present theories, or can be shown to be more questionable than the theories. Excepted from this statement is the diode characteristic, discussed in the previous section.

4. Heterojunctions

There exists very little experimental evidence to provide a check on the validity of the analysis of Emtage for heterojunction cells. Examination of this theory has shown no cause for doubting its validity, however. Since the results indicate that cells with a significantly higher efficiency can not be made by using a heterojunction as the active element, further work in this direction would not appear to be fruitful. It may be expected, however, that other solid state device work will provide new experimental data in this area, and thus the theory will ultimately be tested more directly.

5. The Drift-Field Cell

The analyses of Wolf and of Cheslow, Kaye, and Rolik, to determine the effect of a base region drift field on the collection efficiency in silicon solar cells, are in qualitative agreement in their general conclusions. Direct comparison of the results is not really possible, since very different values of minority carrier-lifetime were assumed for the base region, and hence the optimum drift region widths calculated by Wolf and by Kaye and Rolik are different. In addition, the two cell models analyzed differ with respect to constancy or variability of mobility and lifetime across the drift region.

Within the limitations of the assumptions contained in the models however, the analyses are believed to be valid, but these assumptions are worthy of some scrutiny. The initial analysis of Cheslow and Kaye, with constant value of μ , τ , and E assumed, can be

taken to give qualitatively correct results, but it is not possible to attach significance to the quantitative results. The later refinement of this approach, however, must be taken to provide numerically the most accurate data obtained to date, but at the disadvantage of using wholly non-analytical solutions which require computer usage. The approximations introduced by Wolf allowed him to obtain analytic solutions, but even in this case the expressions are so lengthy that computer usage is desirable. The two theories are basically identical, except for the refinement of variable μ and τ in Rolik and Kaye's latest version, and should therefore give similar results for similar cases. In particular, Wolf had satisfied himself through a step-approximation to the case of variable material values, that the assumption of constant values did not introduce substantially different results, but rather was on the conservative side with respect to the radiation resistance enhancing effect of the drift field. Unfortunately, the authors did not publish on similar cases. The quality of fit between theory and experiment remains to be proven, since data from real cells have been deficient in specifying accurately the actual band structure and semiconduction parameters of the cells. One may note, however, that the experimental results of Kaye and Rolik (for a cell with an unknown drift field strength) show a quite different performance from that predicted by Wolf even though the agreement between theory and experiment is good for the normal type of cell without a drift field (see Figure 91). The discrepancy is seen to be partly due to a larger difference in J_{sc} between experimental field-free and drift-field cells than is expected theoretically, and partly to a more rapid loss in J_{sc} than is predicted. For the experimental cell with the optimum drift region width (according to Kaye and Rolik's calculations), the results bear very little resemblance to Wolf's theoretical results, and Kaye and Rolik did not show any calculations to compare the results with their own theory. In addition, Wolf's theory shows that the initial collection efficiency (and hence initial conversion efficiency) should be higher in a cell with a wider drift field than in a cell with a narrow drift field. Since this is the converse of the results obtained experimentally by Kaye and Rolik, it appears likely that the cells are not comparable in respects other than drift-field region width, and that any deductions from these experimental results should be made with caution.

In summary, then, it is seen that the two theoretical approaches give results qualitatively in agreement with each other. Both indicate that improved radiation resistance should be obtained with a drift-field cell. The theoretical results do not give a good fit to the experimental results, partly because the experimental drift-field cells have a lower absolute performance than theory indicates. This is most likely due to shortcomings in the experimental cells, and may arise from low minority carrier lifetimes caused by the complex cell fabrication processes, with their multiple high-temperature cycles. It is felt that useful progress in the theory of drift-field cells must await the time when more complete experimental data is available to act as a check on the present theories.

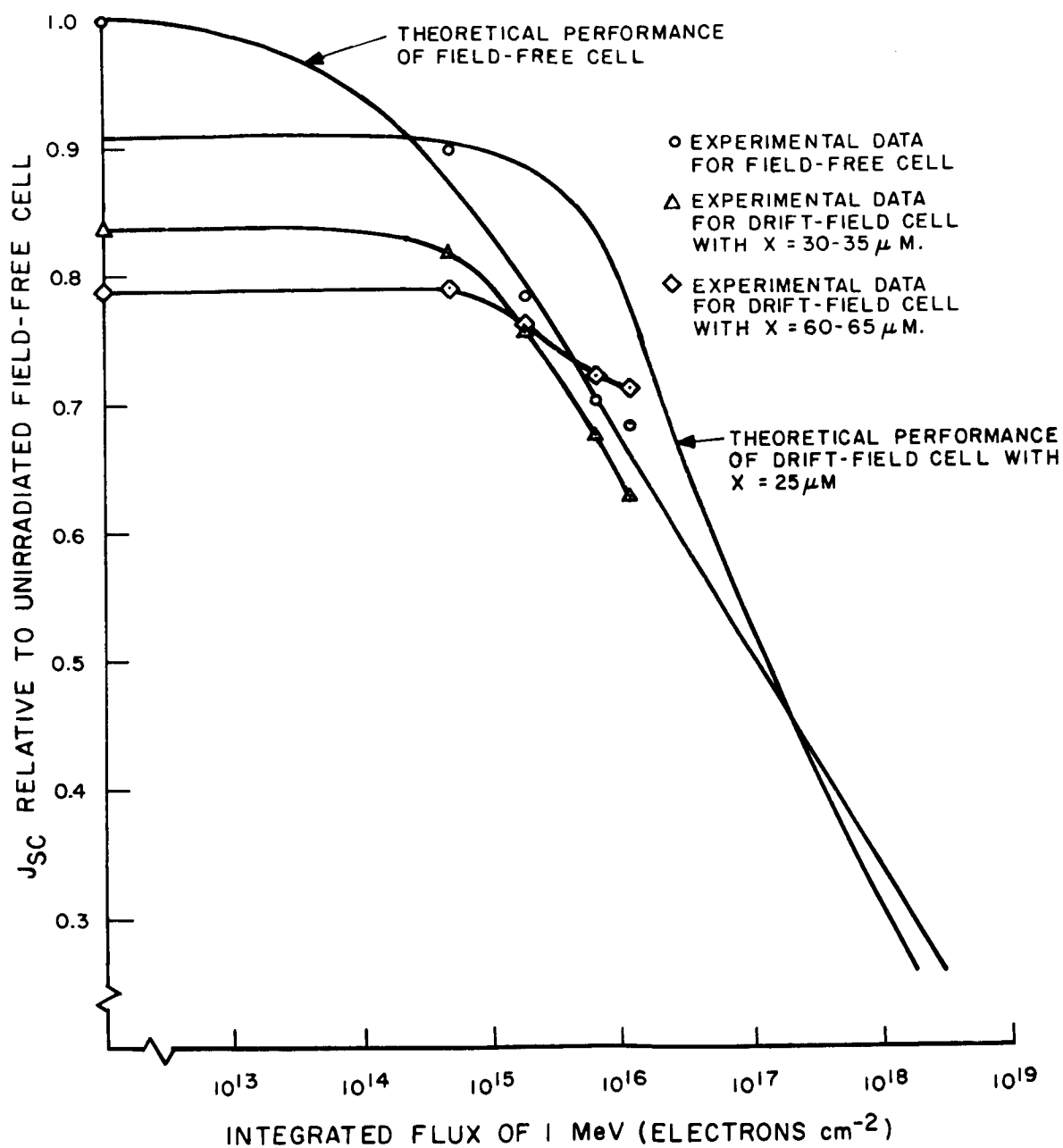


Figure 91. Graph comparing the theoretical results of Wolf with the experimental results of Kaye and Rolik for drift-field solar cells, showing relative J_{sc} as a function of integrated 1 MeV electron flux.

6. The Multiple-Transition Cell

The multiple-transition solar cell, proposed by Wolf in 1960 as a means of obtaining a major increase in solar cell efficiency, has not yet been thoroughly investigated experimentally. Various phenomena observed in CdS and GaP photovoltaic measurements have been explained in terms of transitions induced via intermediate levels, but this explanation is of doubtful validity in the case of the CdS cell, and involved a thermally-induced transition in some of the GaP devices (see IV-C-2 above). The only theoretical work on the principle involved has been that given by Wolf, which does not go far enough to establish unequivocally the validity of the proposal with respect to a potential conflict among the requirements imposed on the material properties. Doubts on this subject were included in Wolf's original publication, and have been repeated by Shockley and others, mainly because experience indicates that the introduction of the needed density of intermediate energy levels ($10^{18} - 10^{19} \text{ cm}^{-3}$) is likely to degrade the semiconductor properties, in particular the minority carrier lifetime. On the other hand, Grimmeis was convinced that he had fabricated photodiodes based on this principle. There are thus questions concerning the principle, through yet unexplored theoretical relationships between material parameters as required for this approach, and, in the absence of such theoretical limitations, the ability to achieve such material properties in a practical device. However, this is the only proposal in existence which shows a possible way towards greatly improving conversion efficiency, and hence it is considered that further investigation would be justified.

It appears that the most pressing immediate need is for theoretical work aimed at providing an answer to the question: can compatibility of the postulated material parameters be proven or disproven by present or modified semiconductor recombination or thermodynamic theory?

In view of the present reservations concerning recombination and junction theories, as discussed in Section V-B-1 above, it may be that unequivocal answers to this question will not be available quickly. However, even an answer of limited validity could be very valuable to indicate whether or not experimental work would be justified.

It should be stressed that even if proven theoretically feasible, the practical realization of a multiple-transition solar cell is likely to require a considerable research effort in terms of both time and money. Because of this, it appears that experimental work will be justified only after investigation of the theoretical question. Although open theoretical questions exist, and although practical realization will, if feasible, be costly, this approach appears to be the only possibility for achieving a marked improvement in conversion efficiency, and hence the potential return on the research investment is sufficient justification for work in this area.

C. SILICON CELLS

Before discussing the work on silicon cells a brief summary of the present status of the cells is necessary. Table IX summarizes the present status with regard to physical characteristics, cell performance, and cell economics.

TABLE IX. PRESENT STATUS OF SILICON CELLS

I. Cell Physical Characteristics
Base Resistivity: 1-2 Ohm-cm, 10 Ohm-cm Cell Thickness: 8-14 mils Configuration: N/P Junction Depth: 0.25-0.50 μm Grid Lines: mostly 5 on cells with 2 cm n-contact length Antireflection Coating: SiO_2 900-1100 \AA , or phosphosilicate glass Dimensions: 1 x 2 cm^2 ; 2 x 2 cm^2 ; 2 x 6 cm^2
II. Cell Performance
Efficiency: Average: AM1-13%, AMO-11%; Max. 14 to 15% (AM1) Short Circuit Current: AM1-29 to 35 mA cm^{-2} , AMO-34 to 40 mA cm^{-2} Open Circuit Voltage: 0.54 to 0.57 V for 10 Ohm-cm; nominal resistivity 0.57 V to 0.61 V for 1 Ohm-cm; nominal resistivity Fill Factor: 73 to 76% Power to Weight Ratio: 95 W lb^{-1} (bare cell; 12 mil thick) Series Resistance: 0.25 to 0.6 Ohms Reverse Saturation Current: 10^{-7} A cm^{-2}
III. Cell Economics
Dollars per Cell: Near \$2.00 ea (1 x 2 cm); near \$3.00 ea (2 x 2 cm) Dollars per Watt: \$60 watt^{-1} - \$80 watt^{-1} bare cell cost

The silicon solar cell has been far more extensively developed than cells made from any of the other materials. This has been partially due to the fact that developments in silicon technology from the relatively large semiconductor device industry were also beneficial to solar cell development, and partially due to extensive work by solar cell manufacturers and photovoltaic specialists. The unique position of the silicon solar cell (availability from going production lines, with adequate efficiency and reliability) at the inception of the space age placed it one step ahead of the other types of cells for satellite applications, and this advantage has continued until the present.

The following evaluation of the work on silicon cells will be broken down into the categories which were used in discussing the history of the silicon cells; i. e., power density, cost, radiation resistance, and efficiency.

1. Power Density

An increasing concern with lightweight solar arrays has derived from the need for increasingly larger amounts of power in current and projected space projects. From the solar cell manufacturers' point of view this concern translates into a need to develop cells with a high power to weight ratio. Since efforts to increase efficiency have, during the last few years, proven fruitless, the approach which appears most feasible at present is the use of thinner silicon wafers in cell manufacture.

Thin silicon cells, on the basis of theory, are expected to have lower short circuit currents than cells of conventional thickness. This drop is due to the loss of some long wavelength photons by transmission, and the closer proximity of the back contact, which has a high surface recombination velocity, to the junction.

Wolf and Ralph (219) published theoretical curves giving the percentages of available photons absorbed by a given thickness of silicon and the relative short circuit current as a function of cell thickness and bulk lifetime. Unfortunately their experimental data did not agree with the theoretical curves. A much more rapid fall off in short circuit current occurred than was anticipated. It was suggested that the cause might be reduction in the effective thickness of the cell due to work damage at the back surface. Adjustment of the data for a change in thickness of a constant amount does not, however, eliminate the discrepancy, although it reduces it somewhat. Crabb and Treble's (221) data agrees more closely, although not completely, with theory. They attributed their success to care in eliminating such damage at the back surface, but it is not clear from the publication what steps or processes were involved, nor why their results should differ from a change in effective thickness. Their results might indicate that the degradation is due to some processing parameter which could be controlled to some extent.

The work of Cheslow and Kaye at EOS indicates that the effect of the high surface recombination at the back contact may be reduced by incorporating a drift field in the

base region of thin cells. Four mil thick drift field cells were found to have 6%-18% higher short circuit current densities than similar cells without drift fields. A simplified theoretical analysis confirmed that gains of this magnitude could be expected. This may be an area of interest for future thin cells work.

The alloyed aluminum reflecting contacts investigated by Burrill et al (294), improving infrared absorption through light reflection at the back contact, also appear to have some interesting effects on the efficiency of thin silicon cells. Cells made with the reflecting contacts also show an increase in effective minority carrier lifetime which could be attributed to a reduction in the surface recombination velocity at the back surface due to formation of a p⁺ region, which means incorporation of a drift field, or to some other lifetime preserving mechanism. There is a striking agreement between the theoretical curves of Wolf and Ralph and the experimental data obtained from some of the reflecting contact cells, although the theoretical curves should not be applicable to these particular conditions.

Thin silicon cells appear to offer advantages as high power density (power per unit weight) devices. Although the ultimate efficiency limitations of some of the thin-film cells are presently unknown, and forecasts are therefore difficult to make, it can be stated that at present the thin silicon cells are quite competitive with these cells on a watts per pound basis (see Figure 58, Section IV-B-3). The thin cells, because of their reduced red response, are more radiation resistant than the thicker cells. Recent measurements have confirmed that the thinner cells do, in fact, deliver constant power over larger ranges of integrated radiation fluxes. In the important area of reliability, the thin silicon cell has presently a distinct advantage over the thin-film cells. Future developments in thin-film cells could negate this advantage; however, reliability has been a longstanding and frustrating problem with these cells. Finally, silicon cells 0.004" or less in thickness possess a small amount of flexibility which, while not generally comparable to that of the thin-film cells, may prove useful in handling and in application. When the hyperdegradation of the short circuit current with thickness and the handling problem of the thin cells can be overcome, then thin silicon cells can be expected to dominate the future solar cell array market.

2. Cost

Attempts to reduce the cost of solar cell manufacture fall into essentially two categories; reduction of materials cost and reduction in cell fabrication cost. Contributions to the reduction of materials cost include refinements in the techniques for producing and purifying the raw silicon and improvements in the growth of single crystal ingots. These changes have been, for the most part, evolutionary as have most of the production line changes which have resulted in reducing cell fabrication costs. Two somewhat more revolutionary changes which have been suggested for cost reduction are the use of polycrystalline material and the use of larger area cells.

The problems connected with the use of polycrystalline cells were found to include lower efficiencies, lower yields, and increased fragility, resulting in increased breakage. The economics of polycrystalline cell use has been best summarized by Berman and Ralph (281), as described in Section IV-B-3. It was determined that a yield of about 80% (i. e., 80% of the cells produced must have efficiencies $\geq 10\%$) is necessary for the polycrystalline cells to break even in cost with the single crystal cells (93-96% of single crystal cells had efficiencies of 10% or greater). Unfortunately no yield data have been given on the polycrystalline cells. Pilot line runs reported by Berman and Ralph indicate that most of the P/N cells had efficiencies in the range 8-10%, while most of the N/P cells were in the range of 6-8%, both airmass 1. The figures indicate that a considerable improvement in the average efficiency of polycrystalline cells is necessary before they can begin to be competitive. The major factors degrading the efficiency of polycrystalline cells are junction leakage and reduced minority carrier lifetime, both associated with the presence of the grain boundaries. A major loss is the drop in open circuit voltage associated with the junction leakage. Open circuit voltages for the polycrystalline cells generally were in the range of 0.45-0.50 volts (vs 0.57-0.60 for single crystal cells). The drop in short circuit density is also of significance. Current densities for the polycrystalline cells were 21-24 mA cm⁻² (vs 22.5-25 mA cm⁻² for single crystal control cells). Obviously these losses are a function of the density of grain boundaries and are therefore variable from cell to cell. At present there appear to be no good prospects for a technique to "neutralize" the grain boundaries. Until such a process is found it is expected that poor yields and low efficiencies will continue to plague the polycrystalline cells and will probably preclude their general use. Some techniques for increasing the resistivity of the material in the vicinity of the grain boundary to reduce leakage have been suggested but these would not solve the lifetime problem and would probably involve extra processing (at extra cost). In general the polycrystalline cells must of necessity be less efficient than single crystal cells. As a consequence, even if the polycrystalline cells can be made competitive with single crystal cells on a dollars per watt basis from the manufacturing standpoint, the use of polycrystalline cells will probably incur additional weight and area penalties which could negate the original cost savings.

The technique of fabricating larger area cells to reduce the production cost per watt has received considerable attention. Much of this has centered on ways of producing large sheets of single crystal silicon. Many of the earlier ideas along this line were patently unfeasible and have since been abandoned. Two ideas which have survived and which show some promise are the epitaxial growth technique and dendritic growth. Epitaxial films of fair quality have been successfully deposited on silicon and sapphire substrates. No reports of success with removable substrates have been found. Whether or not the process can be used to economically produce sheets of adequate thickness and area on a production line basis cannot be determined at this time because of insufficient data. This technique is still in the earliest stages of development and considerable effort will be required before it can be seriously considered for large area solar cell applications.

The most successful technique to date has been the dendritic growth technique. Cell areas of 30 cm² have been realized, with efficiencies as high as 11.5% using this technique. At present the difficulties hindering the use of this process in production include a serious lack of physical uniformity in grown material, high dislocation densities in some regions of the crystal, and a chronic breakage problem associated with the physical handling of the cells (294). The lack of physical uniformity is due to difficulty in controlling the growth parameters (i.e., temperature gradients in the vicinity of dendrites, pull rates, etc). Thickness variations of a factor of two and large width fluctuations on a given sheet of dendritic material are not uncommon. This leads to considerable difficulty in designing jigs and fixtures for handling the material. This control problem is not atypical of problems encountered during process development, and one would expect that, given sufficient developmental time and effort, it could be overcome.

Areas of high dislocation density occur in the filet and twin-plane regions of the dendritic sheet (see Figure 56, Section IV-B-3). These act as recombination centers, thereby lowering collection efficiency, and, in the case of the filet region, contribute to junction leakage. Whether or not the crystallinity in these regions can be improved and controlled as better processing controls are developed remains to be seen. The problem with the filet region is presently eliminated by removing this material in the process of cutting the dendritic sheet to a uniform width. This procedure may not be desirable in future cells because of the breakage problem. Improvement in the quality of the material in this region then assumes a new importance.

Burrill et al (294) have attempted to solve the breakage problem by allowing the dendrites to remain attached to the silicon sheet during cell processing. The dendrites significantly increase the strength of the sheet, but their retention also means that the non-uniformity and leakage problems discussed above become more serious. Despite the increased strength afforded by the dendrites, a 42% breakage rate was experienced. This breakage rate, combined with relatively poor efficiency, indicates that this procedure is highly unsatisfactory at present. The correct line of action to bring the breakage problem under control would seem to be to design the proper jigs, etc., to reduce handling to a minimum. From a production point of view this will probably be the only satisfactory approach. This means that the growth procedure must be brought under control so that the uniformity of the silicon sheet can be insured.

A cost comparison between conventional silicon cells and large area dendritic cells or other large area cells is not possible at this time. However, it has been demonstrated that large area cells offer a reduction in handling costs both in cell manufacture and array assembly. The large area cells have the drawbacks of being subject to more breakage than conventional cells and a possible decrease in array reliability when they are used. If the trend toward larger solar cell arrays, to meet increased power demands in space, continues, the use of thin large area cells will probably be the most economical way of constructing the arrays.

3. Efficiency

The various power loss mechanisms, both inherent and due to departures from ideal behavior, have been discussed in Section IV-A-3 above. The results of this discussion, together with quantitative estimates for the various losses as they occur in present silicon solar cells, are summarized in Figure 92.

The upper limit on efficiency for silicon solar cells has been at a virtual standstill for the past 7-8 years. The last major improvement occurred as a result of the introduction of grid lines at the turn of the decade. Since then the maximum observed efficiency has remained just below 15% while the average efficiency has gradually crept up to about 13%. The average characteristics of current cells have been summarized in Table IX of this section. Table X summarizes the approximate maximum observed values of various solar cell parameters as determined by scanning the published literature and government reports. Slightly better values may have been observed in some cases, however, the values given are probably very close to the maximum. Values of the same parameters as given by or computed from the theories of Shockley and Loferski are also shown.

TABLE X. COMPARISON OF THEORETICAL AND OBSERVED CELL CHARACTERISTICS (AM1)

Parameter	Experimental	Theory (1)	Theory (2)
Efficiency	15%	31%	22%
Short Circuit Current	35 mA cm ⁻²	44.5 mA cm ⁻²	44.5 mA cm ⁻²
Open Circuit Voltage	0.61 volt	0.80 volt	0.58 volt
Fill Factor	0.78	0.87	0.84
Reverse Saturation Current	10 ⁻⁷ -10 ⁻⁸ A cm ⁻²	5.4x10 ⁻¹⁶ A cm ⁻²	5.9x10 ⁻¹² A cm ⁻²
Theory (1) is the detailed balance theory of Shockley			
Theory (2) is the semi-empirical theory of Loferski			

The theoretical values for the open circuit voltage and the fill factor were computed from the values of the other parameters given. Several interesting comparisons may be drawn from this Table. First of all there is a large disparity between all three reverse saturation currents. The reason for this is that Loferski's value was computed from empirical data with the assumption that ideal diode theory was obeyed. Shockley's value was computed from detailed balance considerations assuming only

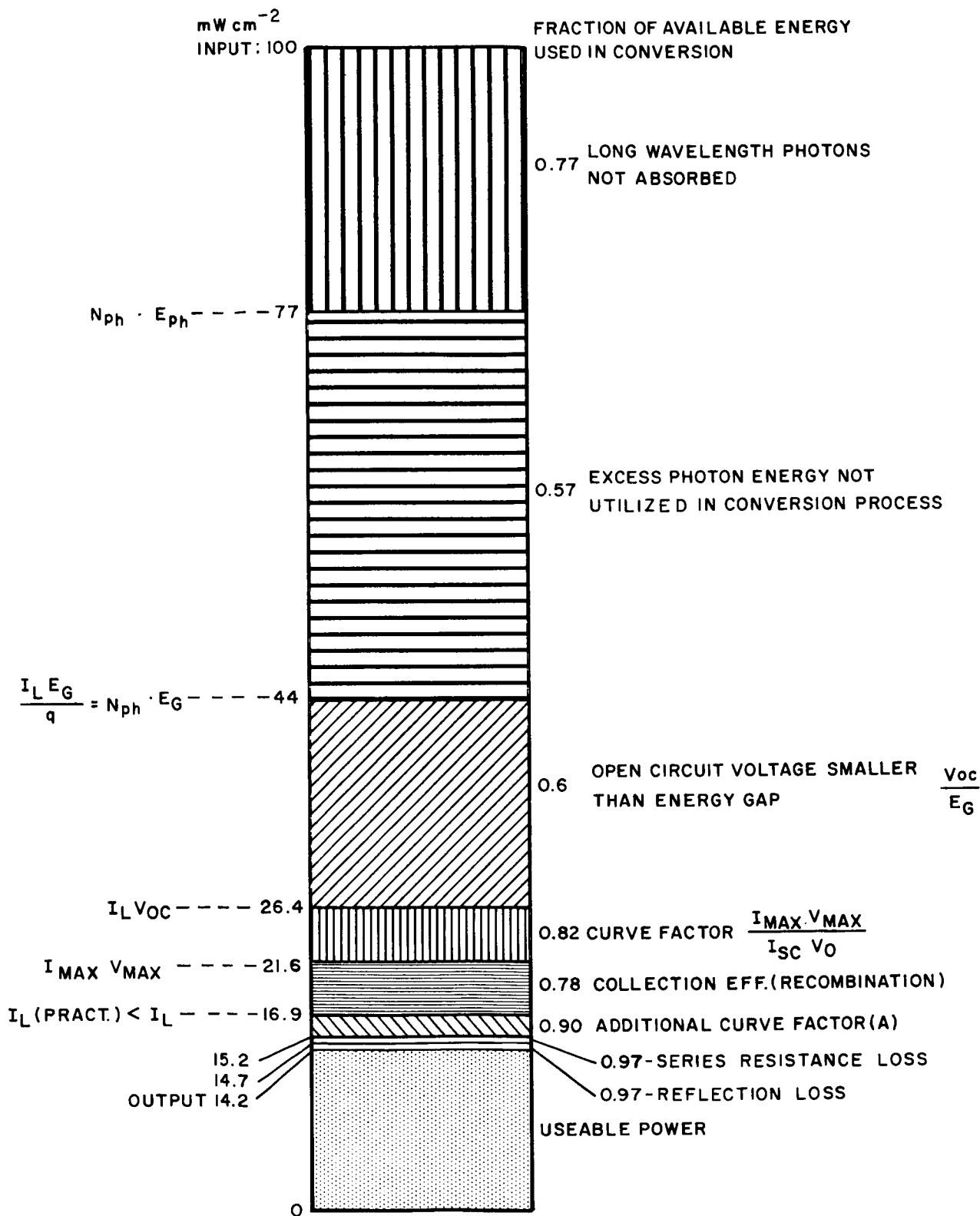


Figure 92. Energy budget for silicon solar cell under AM1 conditions.

radiative recombination. Experimentally the silicon solar cells have been found not to obey ideal diode theory in general, resulting in much larger reverse saturation current values. Computations based on a comparison of the experimental saturation current value and that predicted by theory (1) indicate that the fraction of the recombination-generation current which is radiative is of the order of 10^{-9} in the experimental case. If this could be raised to 10^{-3} or better (i. e., if the non-radiative recombination could be reduced by several orders of magnitude) then theory (1) predicts that the 22% efficiency figure of theory (2) can be achieved.

The open circuit voltage computed from theory (2) is somewhat less than some presently observed figures. This is possible because of deviations from the ideal diode theory. The theory (2) open circuit voltage was computed using the ideal diode value of unity for the diode constant. If a nonideal value of two is assumed then an open circuit voltage in excess of that predicted by Loferski's theory can be obtained despite a difference of five orders of magnitude in reverse saturation current. The experimental and theory (2) open-circuit voltage are approximately 75% of the voltage predicted by theory (1). Again the difference can be traced to the predominance of non-radiative recombination.

There is a difference of at least 25% between the experimental and theoretical short circuit currents. This is by far the largest contribution to the discrepancy between observed efficiencies and the two theories. The theoretical short circuit current value was determined by assuming that all photons with energies greater than the silicon band gap were absorbed and generated hole-electron pairs, all of which were collected. A small percentage of this loss (approximately 1-3%) is attributable to reflection. The remainder is due to recombination of minority carriers before they can be collected or separated by the junction.

The experimental fill factor is seen to be close to that computed from Loferski's theory. This is a result of the minimizing of series resistance effects in current cells, and the continued maintenance of high shunt resistance.

The major problem preventing the realization of theoretical efficiency values is seen to be the high non-radiative recombination rate. This has been pointed out by several investigators in the past (197). The attempts to come to grips with this problem include the use of high purity silicon and the use of special techniques for leaching out metallic impurities. Ralph and Biekofsky (249) used high purity (grade I) silicon instead of the normally used solar grade material in an attempt to make more efficient cells and found that the efficiencies of the higher purity silicon cells were less than those of the control cells made from solar grade silicon. The low efficiency was apparently due to lifetime degradation caused by heavy doping of the high purity silicon. In various attempts to use high purity starting silicon, improvements in solar cell performance or reduction in recombination were not achieved.

Queisser, Shockley, and others (197) have attributed high recombination currents to centers formed by metal precipitates present in the space-charge region of the cell. These currents were held responsible for the anomalous current-voltage characteristics of solar cells. Gettering experiments using glassy oxide layers to remove metallic impurities resulted in improvements in the current-voltage characteristics of the experimental cells, thus indicating that the metallic impurities can be a contributing factor.

While non-radiative recombination is clearly established as a major performance limiting effect in silicon solar cells, the solution to the problem of what can be done to reduce it is not at all clear. This is primarily because the nature of the recombination problem is not well understood. Which species are operative in the recombination process? What is the role of various lattice distortions, such as dislocations? To what degree are the recombination centers present in the grown crystal, and how many are introduced or removed during processing? Are the recombination rates which are now generally obtained in silicon device processing, and which are similar to those obtained in silicon solar cells, the practical limits not to be exceeded through future efforts? These are questions which cannot be answered at present but which must be answered if cell efficiencies are to be significantly increased. It is apparent that the present understanding of recombination processes and their relation to the current voltage characteristic is inadequate.

Additional proposals to increase silicon solar cell efficiency have dealt with various schemes for utilizing regions of the solar spectrum which do not ordinarily contribute significantly to the current, or for making more efficient use of the spectrum. Both Hoffman Electronics Corp. (300) and Technical Operations Inc. (301) investigated techniques for converting high energy photons to multiple low energy photons through the use of fluorescing layers on the surface of the cell. None of the materials used resulted in any measurable improvement in cell performance and in most cases a distinct drop in performance occurred upon application of the fluorescent material. The effectiveness of these materials is greatly impaired by the fact that they also absorb and scatter some of the longer wavelength radiation which normally contributes to cell output. In addition, the efficiency of conversion of high energy photons to low energy photons which actually reach the cell is limited by a number of processes, including scattering and the isotropy of the fluorescent photon emission process. Thus, it appears that the method a priori does not offer any significant potential for improving the efficiency of silicon solar cells.

The Technical Operations group also investigated the possibilities of using dye sensitization techniques to increase response in both the short wavelength region (0.30-0.45 μm) and the long wavelength region (greater than 1 μm). The attempts to improve the short wavelength response by dye sensitization were somewhat misguided in that the problem is not that the radiation is not absorbed by the silicon, but that it is absorbed near the surface of the cell, which has a high recombination velocity, and that

it is absorbed at a considerable distance from the junction, relative to the diffusion length, in material with low lifetime. Hole-electron pairs created in or near the dye layer are still under the influence of this surface region and, unless the dye greatly alters the properties of this region, no gain can be expected from this technique. Similar considerations apply to hole-electron pairs generated by long wavelength photons in surface dye layers, although in this case the photons would not ordinarily be absorbed by the silicon. The dyes also scatter and attenuate radiation to which the cells normally respond, as do the fluorescent materials.

The prospects for success in using surface layers of dyes, phosphors, and other chemical sensitizers to broaden the spectral response of silicon solar cells are very low. Other schemes for altering the spectral response, such as the multiple transition solar cell, have been discussed elsewhere in this report.

Series resistance effects, grid line spacings, junction depths, reflection losses, etc. have all been fairly successfully minimized or optimized and no large improvement in efficiency can be anticipated from these directions.

The rate of recombination appears to be the most important parameter limiting the performance of present silicon solar cells, although an improvement there would increase the cells' radiation sensitivity.

4. Radiation Resistance

The work on radiation resistance has not been treated as thoroughly as some of the other aspects in this account of the history of solar cells. Therefore, a complete evaluation of all of the work in this area cannot justifiably be given. There are three areas of contemporary interest within this field which will be briefly discussed. These are drift field cells, lithium diffused cells, and the "super-blue" cells.

The drift field cells have been shown theoretically (218, 236) and, with considerable reservation, experimentally (290) to have superior radiation resistance to field free cells for many types of radiation. The reservation is inserted because in the experiments the radiation performance of the drift field cells did not correlate with the theory and was found to be only marginally superior to that of the field free cells. This result has to be attributed to deviations in structure and of the experimental devices from the theoretically determined one, and in quality from that normally obtained in production devices. Many of the experimental data were clouded by the presentation as relative short circuit current or power degradation, where actually the absolute power output after a given radiation dose is the important parameter. This would explain why some measurements have shown the drift field cells to be distinctly more radiation resistant than commercially available field free cells, while comparison with field free cells fabricated from the same material as the drift field cells

showed a considerably smaller advantage. This would indicate that the experimental control cells were of lower quality than the commercial cells, and the same doubt would then be cast on the drift field cells. Based on this state of affairs, the merit of the drift field cells can neither be considered proven or disproven, and, depending on the outcome of the lithium - silicon solar cell development, further drift field cell investigations may or may not be undertaken.

A problem facing drift field cells, is the fact that all of the techniques for forming the drift field region require special processes which could add considerably to the expense of solar cell production. Unfortunately, there appear to be no cheap alternatives available; consequently, reducing the cost of existing techniques by proper tooling would seem to be the indicated course of action open at present. The problems involved in controlling epitaxial depositions over large areas, however, may be formidable for some time. The advantages of drift field cells must be more clearly established before the problems of cost should be attacked.

Thin silicon cells have been shown to have increased radiation resistance. Their spectral response is effectively "blue shifted" because the long wavelength photons are transmitted. Thin cells with drift field base regions are of potential interest for use in large scale arrays. Detailed discussion on this subject appeared in Section V-B-5 above.

The lithium diffused solar cell is probably the most important and the most controversial recent development in the photovoltaic field. The cells have been shown to possess the ability to anneal radiation induced defects at room temperature. Uncertainty still exists in discussing the physics of the annealing process, the comparative performance of lithium diffused and commercial N on P cells, and whether or not the lithium diffused cells degrade after recovery. Lithium diffused cells are presently undergoing extensive laboratory investigation intended to provide a thorough understanding of the processes involved and to answer many of the questions regarding their performance. Present indications are that the post-recovery degradation is not inherent to the lithium diffused structure but that it does occur in varying percentages (ranging from the majority to none) of the cells having lithium doping, depending on the type of silicon used and the amount of lithium present. None of the suggested causes for redegradation such as precipitation, out-diffusion, etc., has yet been definitely established as being responsible. Ideas concerning the recovery mechanism are similarly in a state of flux so that it is difficult to say anything definitive in this area except that the generally held view is that it involves a pairing between a lithium ion and a lithium-defect complex. The lithium diffused cell is of considerable importance to the space power field, and its investigation needs to be pursued in a highly systematic and practical manner in order for its capabilities to be evaluated and realized in the near future.

The blue shifting of the spectral response of silicon cells was made possible by the introduction of grid lines around 1960. This allowed the use of the shallow junctions

which give rise to this effect, without seriously degrading the cell performance through series resistance effects. The blue shifted cells are more radiation resistant than cells with deeper junctions because the percentage of their total collected current generated by short wavelength photons has been increased due to the closer proximity of the junction to the surface of the cell. The major practical limitation on the reduction of junction depth has been the fact that effects of the surface, due to its close proximity to the depletion region, start to influence the I-V characteristics. Also, the very shallow junctions are more easily punctured and shorted-out during production and post-production handling. This problem can, however, be overcome by improvement in handling methods, while the first problem is a basic one.

Most of the recent work on the development of "super-blue" shifted cells has been done internally by NASA. The work of Mandelkorn (279) combining LOPEX aluminum-doped silicon and silver-cerium contacts is the latest state-of-the-art development in this direction. There is some evidence that these "super-blue" cells might not be as radiation resistant as has been presumed (524), but published data on these cells are minimal and may not be representative of typical cells. Because of the scarcity of quantitative information it is difficult to gauge the merits of future work in this area. A further shifting of the spectral response is, in theory, possible since a significant portion of the short wavelength photons of the solar spectrum are absorbed in the region between the shallowest of present junctions ($<0.3 \mu\text{m}$) and the cell surface. How difficult it will be to further reduce this thickness is hard to estimate. There appears to be no current work by solar cell manufacturers in this direction, but there is a definite need for a wider dissemination of information on work on the blue sensitive cells.

D. COMPOUND SEMICONDUCTOR CELLS

Although some of the research on compound semiconductor cells has been done with funding from private sources, the majority of the work, and all of the large-scale development efforts, have been supported by Government research and development contracts. Hence, in the analysis of progress in this area, we have concentrated on this Government-funded work. It is interesting to note that in the area of compound cells the USSR has been very active, and in several instances the best results obtained to date have been achieved by Soviet groups. This forms a sharp contrast with work on thin-film cells, where the USSR has expended very little effort, and has reported no results comparable with those obtained on CdS and CdTe thin-film cells manufactured in the US.

There have been three major reasons for interest in compound semiconductor cells:

1. Theoretical efficiency analyses (see Section IV-A-2) indicate that materials can be obtained whose energy gap E_g matches the AMO sunlight spectrum better than that of Si, leading in principle to higher conversion efficiencies.

2. The use of semiconductors with E_g values larger than that of Si also should in principle lead to a device which can continue to show reasonable conversion efficiencies at temperatures considerably higher than those at which Si cells cease to give useful amounts of power.
3. The high optical absorption constant which arises from the "direct" bandgap of certain compound semiconductors should lead to a cell which does not need such long minority carrier diffusion lengths as does the Si cell (see V-E-1 below). Since radiation damage occurs mainly by reduction of minority carrier diffusion length, it is anticipated that improved radiation resistance can be achieved in such compound semiconductor cells.

Actual results indicate that the hoped-for increase in conversion efficiency over the values obtained with Si cells is very difficult to achieve. The difference between the maximum theoretical efficiencies for Si cells and the wider-bandgap materials is not large (about 25%, depending on the details of the analysis), and in practice this difference is more than outweighed by losses which reduce the real cell's performance below that of the ideal cell. These losses are caused by various limitations imposed by the present state of materials technology. Thus, the greatest proportion of the research effort in compound semiconductor cells has been concerned with materials and process technology of general application to the semiconductor in question, rather than in problems specifically associated with solar cell fabrication. Because there has been such a general interest in silicon technology throughout the electronics industry, silicon had a flying start over the compound semiconductors. Only in the case of GaAs cells has a program been sustained at a sufficiently high level and for a sufficiently long period, for results to be obtained comparable with those of Si cells. Even in this case, the technology was in good part supported by general industrial interest in GaAs.

For AlSb, for instance, such general interest has been almost wholly absent, so that success with AlSb solar cells could be expected to be a long uphill battle, even without the very special difficulties encountered with this material.

This phenomenon has been so general throughout the work on compound semiconductor cells that it appears highly unlikely that a future development effort aimed at replacing silicon cells could be economically feasible. The expenditure needed to raise the technology of any semiconductor material to the necessary level would require such a large investment in research that even if efficiencies higher than those of silicon cells could ultimately be achieved, the cost would be so high as to make the success of doubtful value. This assumes that the cell mechanism is that analyzed in conventional treatments of theoretical efficiency: if a really large increase in efficiency were found to be possible, as in the multiple-transition cell, for instance, then the research investment could certainly be justified.

Considerations other than simply replacing the silicon cell with a more efficient device operating in the same environment may also make compound semiconductor cell development desirable. These would probably be the factors under (2) and (3) above. Unlike the efficiency improvement, these have been verified experimentally, and for several of the cell types it can be shown that photovoltaic arrays could be built to operate under conditions intolerable to silicon cells. Whether or not the value of the missions which require operation under these conditions would justify the necessary expenditure of research and development effort is a question beyond the scope of the present work.

1. Gallium Arsenide

By far the largest effort to develop a single-crystal cell alternative to the silicon cell was spent on GaAs devices. Initial studies at RCA Laboratories, supported by the Signal Corps, were followed by large development and pilotline projects at RCA Somerville, supported by the USAF. Realizing that process and materials technology were the keys to obtaining viable cells, adequate efforts were expended in these areas to result in cells with average efficiencies in the 9-11% interval, and with peak efficiencies up to 13%. Since this is closely comparable with the results achieved with silicon cells, the development program must be considered a technical success.

This program illustrates well the fact that the development of a cell based on a new semiconductor will require a major investment in research areas which are not specifically concerned with solar cells. Thus, after the demonstration of feasibility by RCA Laboratories, the RCA Somerville group had to develop methods for growing ingots of single-crystal GaAs with a cross-section sufficiently large to allow economical fabrication of 1 x 2 cm wafers, and with a quality adequate for obtaining good minority carrier lifetime and mobility. Likewise, methods had to be developed to provide the necessary shallow junctions: this may be regarded as specifically a solar-cell requirement, although general methods for diffusion processing in GaAs were not readily available at the time, so that the development done in this area also had a wider scope than might be at first apparent. Finally, the methods which were developed for providing electrically and mechanically sound contacts to the cells also represent the development of a technology not specific to solar cells.

The results which were achieved demonstrated that the GaAs cells had no advantage over silicon cells with respect to efficiencies at normal temperatures, but that they did have advantages in terms of radiation resistance and high-temperature performance relative to silicon cells as shown in Table XI.

As pointed out by Lamorte, the GaAs cell also has a comparatively constant V_{mp} under irradiation, and this would make the design of a solar power system easier than with Si cells. However, since the GaAs cell work ceased in 1963, the development of the lithium-doped silicon cell has offered the possibility of reducing the radiation damage

TABLE XI. DATA COMPARING RADIATION RESISTANCE AND HIGH-TEMPERATURE PERFORMANCE OF Si AND GaAs CELLS

Parameter	GaAs	Si
Rate of efficiency loss with rise of temperature	0.02 - 0.03 %. (C°) ⁻¹	0.035 - 0.045 %. (C°) ⁻¹
Critical flux of 17 MeV protons	1.5 - 6x10 ¹² cm ⁻²	1.5 - 2.0x10 ¹¹ cm ⁻²

problem in silicon cells so as to remove this as a significant advantage of the GaAs cells. The high-temperature operation of the cells remains a feature which cannot be duplicated by silicon cells, however, and there are physical reasons why this will always remain true (see the account of Shockley's diffusion theory of p-n junction behavior, Section III-D-2).

Several loose ends may be noted among the results reported by the RCA workers. Should the further development of GaAs cells prove desirable, these provide possible areas of investigation.

Although cells were made using epitaxial GaAs layers, their efficiencies were lower than those of conventional cells. However, in the years since the termination of the GaAs solar cells work, processing methods have been developed which allow epitaxial layers of GaAs to be formed in a highly controlled manner, with excellent semiconductor properties (458). The use of epitaxial material therefore offers the possibility of making cells with an active region in which long minority carrier diffusion lengths exist. This should improve the collection efficiency, and further improvement may also be possible if a drift-field cell can be made by providing a gradient of impurity concentration in the active region by control of the epitaxial growth process.

Another point which may be again worth taking up would be the use of the n-on-p in place of the p-on-n configuration used in the majority of the cells. This point was investigated during the original work, and low efficiencies were always obtained. It may be that the dopants suitable for use in cell fabrication have solid solubilities which prevent the necessary high doping levels from being achieved: the original work showed that zinc (an acceptor) was particularly well suited to cell fabrication because it produces a high surface concentration and an anomalous diffusion profile particularly advantageous in solar cells. Assuming that a donor species can be found with the same characteristics, the n-on-p configuration would provide a cell with electrons as minority carriers in the base region. Since electrons have a mobility higher than holes by about an order of magnitude in most GaAs, this should lead to improved collection efficiency from the base region. The full benefit of such an effect would not be realized unless

the junction depth could be reduced somewhat from that used in the original cells ($\sim 0.5 \mu\text{m}$), so that the surface region provides only a small proportion of the cell output.

A further loose end left at the termination of the GaAs cells work concerned high-temperature degradation of the cells. The effect seen was a rapid loss of efficiency by V_{oc} degradation when cells with soldered tabs attached were stored at 250°C : the effect was absent from cells without tabs. This implies that the effect was not an intrinsic part of the cell, and could be eliminated by using different contacting materials. Since there are alternatives available for this purpose, this effect cannot be expected to pose an insuperable problem.

One aspect of the operation of the GaAs cells must be considered as extremely interesting. It was reported that V_{oc} values up to 0.96 V were obtained with cells operated under $100 \text{ mW}\cdot\text{cm}^{-2}$ sunlight, presumably at room temperature (317). More details of cell measurements were reported showing V_{oc} values up to 0.94 V for $I_{sc} = 29.2 \text{ mA}\cdot\text{cm}^{-2}$ (330).²⁵ Applying equation (58), this indicates $J_0 = 1.3 \times 10^{-19} \text{ A}\cdot\text{cm}^{-2}$, whereas in theory, $J_0 = 1.5 \times 10^{-15} \text{ A}\cdot\text{cm}^{-2}$ for a GaAs p-n junction. This assumes that $A = 1$ in the diode equation, whereas in the actual cells it was normally approximately 2,²⁶ which could increase J_0 to a value nearly 5 orders of magnitude higher than the theoretical value. However, changes in A and J_0 have been found in Si solar cells to go together in such a way as to produce V_{oc} values lower in practice than or equal to those predicted by the simple diffusion theory ($A = 1$), rather than the slightly higher V_{oc} values measured in the GaAs cells. This may have two implications:

- a. GaAs cell efficiency improvement may be obtained by an improvement in J_{sc} , and this has been more amenable to development than V_{oc} in most types of cell.
- b. If similar effects could be achieved in silicon cells, a considerable improvement in efficiency would result. Thus research aimed at an elucidation of this effect could be a useful contribution to the theory, and perhaps also the practice, of silicon cells.

A major obstacle to the general use of GaAs cells has been their price: GaAs cells cost over an order of magnitude more in terms of dollars-per-watt than the normal Si cells. Assuming the array fabrication to require the same cost in the two cases, and these being approximately equal to the cost of the silicon cells, this reduces the cost differential to 5.5 or larger, which is still high. Although large-scale production

²⁵ p. 119, cell #91-13.

²⁶ This implies that recombination-generation processes in the junction region dominated the junction characteristic (see Section IV-A-1), a point fully discussed in reference 316.

and consistent demand would reduce costs somewhat, it appears that the starting materials in cell manufacture (ultra-high-purity gallium and arsenic) will always be more expensive than silicon. In addition, GaAs has a more difficult technology than Si, making processing more costly. Eg., GaAs has a much lower yield stress than Si, leading to a problem with brittleness, and subsequent loss of cells by breakage. It thus appears that GaAs cells are unlikely to ever compete with Si cells for normal array applications, and only when the special properties of the GaAs cells make these devices necessary will they be considered. This provides an interesting parallel with other device technology for this material, where GaAs has not been able to compete with Si transistors for ordinary purposes. But where the special properties of the material can be exploited, it has found applications like in Gunn effect devices and diode lasers.

The GaP-GaAs heterojunction device investigated by various groups is in principle a sound idea, insofar as it enables one to make a GaAs solar cell with a junction sufficiently removed from the semiconductor surface that recombination will not degrade collection efficiency. In practice, the GaAs cell work showed that the field in the diffused region of the conventional GaAs cell (caused by the diffusion profile) is sufficient to prevent large numbers of minority carriers from reaching the surface. Thus surface recombination is not a major problem in conventional GaAs cells, a finding which closely parallels the effects seen in conventional silicon cells. Thus, the GaP-GaAs cell loses its major *raison d'etre*, and since the use of this configuration complicates a processing technology situation which is already difficult, it is concluded that further work in this area cannot be justified.

2. Other III-V Semiconductors

The work done on pure GaP cells by the RCA and Monsanto groups showed divergent results, for reasons which were not clarified, but which have implications which make further analysis valuable.

The RCA cells exhibited only theoretically anticipated behavior, with an intrinsic spectral response. This exploratory work therefore indicated that the cells' potential efficiency was as calculated by Loferski and others, using the analysis based on p-n junction theory and a spectral response determined by E_g for the semiconductor. In view of the poor match between the GaP bandgap ($E_g = 2.25$ eV) and the sunlight spectrum, the indicated potential efficiency was low, and hence work was not continued. The Monsanto work, however, resulted in two families of cells being made, one showing the intrinsic response as seen in the RCA work, the other cells showing an extrinsic response of the type sought by the RCA group in the first place. It is unfortunate that the Monsanto group was not able to discover what caused the difference in behavior of the two groups of cells, since some of the results indicated considerable potential in the extrinsic-response cells. It appears that the materials and processing difficulties were so large that reproducibility and adequate manufacturing control could not be obtained. This is not surprising, since according to general observation, the wider the bandgap

of a semiconductor, the more difficult it is to make contact to it, and to avoid introducing intermediate energy levels in the forbidden bandgap which can introduce extrinsic semiconductor behavior.

Comparing the results of the Monsanto spectral response measurements with those of Grimmeis on extrinsic GaP photosensitivity, it is apparent that the effects are quantitatively different, although they are qualitatively similar. Hence, the Grimmeis model for the cell mechanism may fit the Monsanto data but with a different intermediate energy level present, or a different mechanism may be at work. The Monsanto work left open the question of the extrinsic response mechanism, which is unfortunate. This work appears to have potential mainly in reference to the multiple-transition solar cell, which has been discussed in Section V-B above.

The Monsanto work clearly established the potential advantage of the GaP cells for operation at high temperature, the V_{OC} values having been found to drop at a rate of about $3 \times 10^{-3} \text{ V.}^\circ\text{C}^{-1}$, close to the theoretical value. The value was about the same in both the intrinsic and extrinsic response cells, and allowed both cell types to operate at temperatures as high as 350°C . The high temperature performance being better than that of the GaAs solar cells discussed above, the same remarks concerning the value of further research can be made. The only difference is one of degree: it seems certain that with adequate effort, GaP cells could be made with efficiencies considerably higher than the 2.5% peak seen in the Monsanto work. However, it should be stressed that the research investment needed would be large, at least as big as the multi-million dollar GaAs cells effort. Whether or not this would be justified by the ability to make arrays which could operate at high temperatures is a question which must be answered by others, unless the feasibility of the multiple-transition solar cell has first been established and the material properties for GaP been found suitable for this type of cell.

The remaining III-V compound on which a large government-sponsored research effort has been concentrated is aluminum antimonide, AlSb. As with all of the other research projects on compound semiconductor cells, this was largely involved with solving quite general crystal growth and materials processing problems. The main justification for interest in AlSb was the closeness of its bandgap match to the solar spectrum, according to the theoretical efficiency analyses. However, the difference between the behavior of ideal AlSb and Si cells is not large, while, in view of the differences in technology which presently exist between AlSb and Si, no reason can be seen for an expectation that practical cells of AlSb might approach the ideal behavior any better than Si cells, so that logical justification for work on AlSb solar cells is not provided.

The EOS research program on AlSb cells was directed almost entirely toward solving the materials problems, and must be considered successful in this respect on the basis of the results which were achieved. Thus, large single-crystal ingots of the material were grown, and slicing, lapping, contacting, and diffusion techniques were established. Although significant solar cell results were not obtained the materials work done by the EOS group appears as a remarkable achievement, bearing in mind the peculiar problems associated with AlSb.

The RCA work on AlSb provides an interesting contrast with this, in that the RCA group bought its material from an outside source, and thus was able to concentrate its energies much more on the problems of cell manufacture. Again considering the problems inherent in dealing with AlSb, the results which were achieved are remarkable. In view of the extremely reactive and unstable nature of the basic material, the spontaneous degradation of the cell performance, which proved the major difficulty, is hardly surprising. Because the effects of moisture absorption are apparently irreversible in the AlSb cell, there appears to be little prospect of stabilizing this device, or of devising practicable manufacturing methods. From this experience, it is concluded that further research on AlSb cells is unlikely to yield useful results.

Indium phosphide (InP) is the remaining III-V compound whose conversion efficiency could in principle be high (Loferski's analysis indicated a value of 21.5% under AMO sunlight). The work done on this material by the RCA group, beginning in 1955, was severely hampered by lack of good single-crystal starting material. Hence good results could not be obtained without a large materials research program, for which support was not available. In the ten years which have elapsed since this early work, compound semiconductor technology has improved enormously, however, so that it seems surprising that there has been no further US work aimed at developing InP cells. The recent reports of the USSR work indicate that good efficiencies (6.7%) have been obtained even with poorly designed (deep junction) devices. Thus it appears reasonable to expect that a materials development program, aimed at producing crystal growth methods and diffusion and contacting techniques, could result in solar cells with useful efficiencies. However, the justification for such a program is questionable. The theoretical efficiency of the InP cell is only marginally better than for Si, and there is no reason to suppose that the technology limitations will allow practical InP cells to approach the ideal performance any better than in the case of Si. The high-temperature behavior would be intermediate between that of Si and GaAs cells, so that this would not be a valid reason for developing InP. Finally, the material has an indirect optical transition, so that the exceptionally sharp optical absorption edge of GaAs, and the radiation resistance which results, will not be obtained with InP as far as can be predicted. So far as is known, the material does not have any special technological difficulties associated with it (cf. AlSb), and the 1.25 eV energy gap is low enough that the provision of ohmic contacts, and the introduction of intermediate energy levels in the forbidden gap, are not likely to cause special difficulties (cf. GaP).

The remaining III-V compounds have energy gaps which will be unsuited to solar energy conversion, so far as is known. Thus, work with these materials cannot be justified at the present time. However, should cell mechanisms other than those analyzed in the conventional theoretical efficiency calculations be proved feasible, then some of these other III-V semiconductors may turn out to have special properties which can be exploited. For instance, the multiple-transition cell would probably be based on a material with a band-gap in the 1.5 - 3.0 eV range, so that a material such as aluminum arsenide (AlAs) with $E_g = 2.4$ eV, or GaAlAs, could well be potentially valuable. Since very little is known about these materials, however, it is not possible to make a meaningful analysis of the likelihood of success with this compound. The only firm prediction which can be made is that the amount of research necessary will be expensive and time-consuming.

3. II-VI and Other Compounds

Cadmium sulfide (CdS) is of course the II-VI material with which most research has been performed. However, for the reasons discussed in V-E-1 below, CdS is particularly well-suited for use in thin-film cells, so that since about 1960, the major research effort with this material has been in the direction of making thin-film cells.

There is another side to this question which will be examined here. Experience has shown that the technology of single-crystal CdS provides special difficulties which make large-scale production unattractive. This is particularly true of crystal growth. Large efforts were expended in this area in the 1955-1960 period, and the results showed that the normal methods for pulling single crystals from the melt were unsuited to use with CdS because of the high melting temperature of the compound, and the high vapor pressure of the component materials (~ 100 atm.) at this temperature. Hence the vapor-phase crystal growth process as developed by Reynolds remained the most practical method for growing large single crystals of CdS. This method is comparatively slow (a single furnace run takes several days), and the furnaces required are large. For research purposes, of course, the process is perfectly good, and with skillful operation can produce high quality material.

The single-crystal CdS cell work done during the 1955-1960 period was mainly significant in developing contacting techniques and barrier formation methods which have since been applied to thin-film cells. More recent work with single-crystal cells has largely been directed toward investigation of the extrinsic photoresponse mechanism. Single crystals have been used to permit tighter control of the cell fabrication processes, and elimination of artefacts introduced by the film growth process, so as not to obscure effects which may give clues to the mechanism of cell operation. While this is a justifiable technique, it must still be applied with care, as evidenced by the widely divergent results which have been reported by different groups who have done research in this area. Even with single-crystal starting material, the cells which are made may have very different properties depending on the fabrication processes used. The validity of applying to thin-film cells conclusions arrived at from results obtained with single-crystal cells has therefore to be carefully checked in each individual case. The approach can be valuable when applied with care, and the results of Shiozawa's work in elucidating cell mechanisms by combining results from single-crystal and thin-film cell experiments are good evidence for this.

Much of the same analysis can be applied to the results which have been obtained with single-crystal CdTe. The early interest served largely as a spring board for the thin-film cells work which followed. The material is considerably better suited for use in thin-film cells than most compound semiconductors, whereas it is difficult to obtain good quality single-crystal material. Thus the main justification for recent work on single-crystal CdTe cells has been as an adjunct to thin-film cell work, to provide guidance towards improving the efficiency and reliability of these cells. Because there are no major uncertainties concerning the mechanism of cell operation, the application of single-crystal cell results to thin-film cells is easier than in the case of

CdS. It is anticipated that future work on single-crystal CdTe cells will be only for research purposes, to support the thin-film cell work, and there appears no reason for initiating work aimed at developing single-crystal CdTe cells for practical application.

Cadmium selenide (CdSe) is the remaining II-VI compound with which single-crystal photovoltaic cells have been made. The same crystal growth difficulties as for CdS are met with in CdSe, so that vapor growth of single crystals has also been used for this material. The cells made have all been barrier-layer devices using metallic or degenerate-semiconductor (Cu_2Se) blocking contacts, since this material forms only one conductivity type (like CdS). Again, conventional efficiency analyses and practical experience combine to indicate that further work with this material is very unlikely to be fruitful.

A host of other compound semiconductors exist, a few of which have been investigated experimentally for use in solar cells, but for most of which no work has been done. Of the former, ZnS and SiC have much wider bandgaps than are advantageous for solar energy conversion, and for SiC the materials technology is made particularly difficult by the refractory nature of the material. For these and for other unexplored compound semiconductors, one must conclude that there exists at present no logical justification for initiating work aimed at making solar cells of these materials. This situation may change if the multiple-transition solar cell is found to be practicable, or if a materials technology breakthrough is made with any of the compounds. However, work aimed at making such a breakthrough is considered to have such a large cost to success-likelihood ratio as to be not logically justifiable at the present time.

E. THIN-FILM CELLS

In an evaluation of results which have been obtained with thin-film solar cells, the usual criteria are naturally applied, such as reduction of device cost, increase in conversion efficiency, and increase in service life. In addition, an objective of much thin-film cell development has been an increase in the power-to-weight ratio. However, this criterion must be applied with discrimination, since in some cases devices have been made which offer high power-to-weight ratios but only modest efficiencies (less than 5%). The most natural application of thin-film cells is to large arrays generating 100 W or more. But if low efficiency devices are used, such arrays become very large, leading to potential problems in deployment, vehicle attitude control, and drag.

Light-weight deployment systems with low rigidity would compound this problem. Such array considerations are strictly beyond the scope of this work, but it is felt that they ultimately provide the criteria by which device performance is judged, and although most of these criteria are well appreciated by device workers, one must conclude from some results which have been published that the need for high power density in thin-film cells has not been stressed sufficiently.

1. Comparative Studies

Before beginning a detailed analysis of individual thin-film cell types, it is felt that a comparison between the three major cells will provide a perspective in which individual performance can be judged. The three cells in question are those based on cadmium sulfide (CdS), cadmium telluride (CdTe), and gallium arsenide (GaAs).

Although some early work has been performed towards thin-film silicon solar cells, this material, being an indirect semiconductor, is clearly not a suitable material for thin-film solar cells, unless some other absorption mechanism can be utilized. CdS and CdTe are compounds made from elements in group IIB and VIA of the periodic table, and are hence termed II-VI compounds. For a similar reason, GaAs is termed a III-V compound. This classification is useful, since the properties of the II-VI compounds exhibit characteristics in common, and sharply different from those of the III-V compounds. From the point of view of the present discussion, the most important difference between the two groups is the ease with which thin layers of the compounds can be formed. This arises from the greater volatility of the elements comprising group IIB of the periodic table (Zn, Cd, Hg), compared with that of the IIIA elements (Al, Ga, In).²⁷ The least volatile IIB element, Zn, has a vapor pressure almost nine orders of magnitude higher than the most volatile IIIA element, In, at the same temperature. Since the evaporation of these compounds proceeds by dissociation into the elements followed by their evaporation, the volatility of the elements determines the temperature at which it is necessary to run a vacuum evaporation source. Most importantly, however, the same consideration governs the minimum substrate temperature at which good crystallinity will be obtained in a deposited film. This occurs because the substrate must be at a temperature sufficiently high that atoms which are not bonded initially into a crystallographically correct position on the growing surface (which will in general be a position of minimum potential energy) can be re-evaporated, or have sufficiently high surface mobility to move to a correct position. For this reason, thin films can be deposited from the II-VI compound with the most volatile components, CdS, by vacuum evaporation from a source at a conveniently low temperature onto a substrate at a temperature which is also relatively low, 200-300°C: hence plastic substrates are possible for CdS cells. CdTe, with a slightly lower volatility, must use a correspondingly higher substrate temperature, 300-400°C, and a plastic film capable of withstanding this temperature is not yet available. For GaAs, the film growth temperature is much higher, 700-800°C for really good results. Experience thus indicates that certain II-VI compounds are easier to use in thin-film devices than certain III-V compounds, and in examining the fundamental reasons underlying this, one concludes that this observation can be extended to all II-VI and III-V materials.

The active junction formation method, and the nature of this junction, provide a second point of comparison between the thin-film cell types. It has not been found advantageous

²⁷Other elements exist in these groups, but these do not form semiconducting compounds of potential interest for solar cell fabrication.

to use diffused p-n junctions of the type used in single-crystal cells in any of the polycrystalline thin-film devices. This is again a metallurgy related question, it being found that solid-state diffusion of impurities, as is generally used to form p-n junctions, proceeds more rapidly along the intercrystalline boundaries than through single-crystal regions. This expected result has been demonstrated experimentally by Queisser (525). Since thin films of semiconductor are polycrystalline when formed on glassy or microcrystalline substrates, as is normally done, thin-film cells contain large numbers of grain boundaries. Thus, solid-state diffusion occurs in a very non-uniform fashion in such material, which leads to junctions of poor quality. These are generally observed as leaky diodes, the good junction area in the single-crystal regions inside the grains being shunted by leakage paths occurring at the grain boundaries. The result is a low V_{oc} value, as was obtained in the work on GaAs thin-film cells, for instance. It has frequently been the hope of those working on the development of thin-film cells that p-n junctions could be formed either by changing the dopant during film growth (one processing step), or by growing successive layers of different conductivity type (two processing steps). This has not so far led to good results, which appears to be due to the fact that the substrate temperatures during film growth are sufficiently high to lead to solid-state diffusion. Thus, the junction which would in principle form by growth of successive layers of differing conductivity type, is in practice modified by preferential diffusion along grain boundaries, leading to the results discussed above.

These results have led the thin-film cell workers to use other types of active junctions. In principle there are two possible alternatives:

- a. a heterojunction, in which a layer of semiconductor is formed of a material different from that forming the base, or
- b. a surface barrier junction, in which a layer of a degenerate semiconductor or metal forms a blocking contact to the semiconductor by the mechanism discussed originally by Schottky and modified by Bardeen (see Sections II-C-2 and III-D-2).

In the heterojunction, the semiconductor with the smaller bandgap governs the long wavelength cutoff of the spectral range of sensitivity of the device, and also the I-V characteristic, and with it the open-circuit voltage, so that this material essentially determines the theoretical efficiency of the cell. However, photons absorbed in either of the semiconductors generate hole-electron pairs which can be separated by the junction and thus contribute to cell output. In the barrier-layer cell, however, photons which are absorbed in the metal or degenerate semiconductor are not expected to contribute effectively to cell output, since the minority carrier diffusion length in these materials is extremely small. Some contribution to cell output will occur, due to photoemission, but this is mostly small in comparison with the output due to absorption of photons in the base semiconductor.

The difference between these two types of junction may account for differences in behavior of some thin-film cell types. Assuming that the "1067" model of CdS cell operation is basically correct, the device would be of the heterojunction type, and carriers generated by photon absorption in both the Cu₂S and the CdS are collected and contribute to cell output. Since the Cu₂S has a bandgap narrower than that of the CdS (1.2 eV, 2.4 eV, respectively), the Cu₂S determines the V_{oc} and spectral response range of the cell, as is observed experimentally. However, in the GaAs cells, photons absorbed in the barrier layer material (platinum, or cuprous selenide) do not contribute to cell output. Although this does not explain all of the difference in efficiency between these two cells, it is a major contributory factor. The CdTe cells appear to behave as barrier-layer devices, since the major spectral response of the cell is that of the CdTe, although the Cu₂Te is a semiconductor with an energy gap smaller than that of the CdTe (1.0 eV vs. 1.45 eV). This indicates that the Cu₂Te does not contribute to cell output. However, Cu₂Te is an indirect bandgap material, with a low optical absorption constant in the range of photon energies between 1.0 and 1.45 eV. Thus the thin layer of Cu₂Te which exists in the thin-film cells does not absorb enough photons to contribute effectively to cell output, even though the minority carrier diffusion length may be adequate to give reasonably efficient collection from this layer. Hence the CdTe cells may indeed contain Cu₂Te-CdTe heterojunctions, as proposed by Cusano, even though the spectral response of the cells is not that of the Cu₂Te. In this case, however, the Cu₂Te bandgap may determine the V_{oc} value as has actually been observed with dip-processed cells (but see the discussion later on this point). This implies that an alternative to the Cu₂Te-CdTe heterojunction, such as a wider bandgap semiconductor heterojunction, or a metal-semiconductor barrier, might provide higher efficiencies in the CdTe cells. In practice this may not be possible, since the Cu₂Te-CdTe heterojunction appears to provide a low density of leakage paths and other degrading mechanisms, in addition to being compatible with the graded copper-doping region at the CdTe surface, which apparently aids the collection efficiency. This point is further discussed below.

It would be desirable to compare the measured performance of the best cells of each type with theoretical maximum efficiency values, derived from analyses of the type described in Section IV-A-2. For each of the major thin-film cell types, however, the structure is not sufficiently well known for a theory to be capable of describing its predicted behavior, and any attempt at accurate comparison would reflect more on the inadequacy of the model chosen than on the lack of development of the cells. However, sufficient knowledge of the working of the cells exists to allow an estimate to be made of their ultimate efficiencies, provided some assumptions are made. This has been done for the three thin-film cell types, and the results are displayed in Table XII. Before discussing the implications of this data, the assumptions underlying the various calculations shall be given. These are sufficient to allow the reader to perform the same calculations.

The experimental data for each cell type were obtained from the published I-V curve for the most efficient cell made, extrapolated to an illumination intensity of 140 mW·cm⁻². The extrapolation proceeded by the following steps:

TABLE XII. COMPARISON OF THEORETICAL AND EXPERIMENTAL EFFICIENCIES IN THIN-FILM SOLAR CELLS

Cell Material	Cutoff Wavelength Å	Data Type	J_{sc} (A · cm ⁻²)	J_o (A · cm ²)	V_{oc} (V)	F	η (%)
CdS	10,500 (Cu ₂ S)	Experiment	34x10 ⁻³	7x10 ⁻¹¹	0.50	0.69	8.35
		Theory	51x10 ⁻³	10 ⁻¹⁴	0.73	0.85	23
		<u>Experiment</u> Theory	0.67	-	0.68	0.81	0.36
CdTe	8,500 (CdTe)	Experiment	24x10 ⁻³	2.2x10 ⁻¹²	0.58	0.65	6.5
		Theory	39x10 ⁻³	10 ⁻¹⁹	0.95	0.89	21
		<u>Experiment</u> Theory	0.62	-	0.61	0.73	0.31
GaAs	8,750 (GaAs)	Experiment	21x10 ⁻³	4.7x10 ⁻¹¹	0.50	0.57	4.2
		Theory	41x10 ⁻³	10 ⁻¹⁶	0.84	0.87	21
		<u>Experiment</u> Theory	0.52	-	0.60	0.65	0.20

a. from experimental V_{oc} and J_{sc} values, J_o was obtained from:

$$J_o = J_{sc} \exp \frac{-qV_{oc}}{kT} \quad (132)$$

This step therefore assumes $A = 1$ in the diode equation. Although this is known to be not a valid assumption, it has been made for two reasons:

- (i) it is common experience that J_o and A depart from theoretical values in such a way as to compensate each other, and thus efficiency calculations are not greatly affected.
- (ii) values of J_o and A are almost never published, so that some unifying assumption must be made to allow comparison between different cells.

- b. J_{sc} at $140 \text{ mW} \cdot \text{cm}^{-2}$ was calculated by directly scaling the experimental J_{sc} value. This step assumes that the short circuit current varies linearly with light intensity and that the R_s effect can be neglected. This assumption is necessary since R_s values are not normally published for cells. In the best cells of each type, R_s effects are not very large, and this assumption does not cause a disproportionately large loss of accuracy compared with other approximations in the calculation.
- c. From the J_0 and J_{sc} value at $140 \text{ mW} \cdot \text{cm}^{-2}$, V_{oc} at $140 \text{ mW} \cdot \text{cm}^{-2}$ was calculated from the inverse of equation (132):

$$V_{oc} = \frac{kT}{q} \ln \frac{J_{sc}}{J_0} \quad (133)$$

The assumptions here are the same as those in paragraph a., above.

- d. The fill-factor F was calculated from the published experimental curve, and was then used in conjunction with the extrapolated V_{oc} and J_{sc} values to calculate an extrapolated experimental efficiency at $140 \text{ mW} \cdot \text{cm}^{-2}$. This also makes the assumptions of paragraph b., above, although the remarks on the error introduced do not necessarily apply, since the effect of R_s is much larger near the maximum power point, and is generally not negligible in even the best thin-film cells.

The theoretical calculations were performed as follows:

- a. J_0 was calculated from Shockley's diffusion theory, using data on carrier lifetimes and mobilities as measured for silicon, but with E_g appropriate to the cell under consideration:
 - (i) For CdS cells, the V_{oc} was taken to be governed by the energy gap of the Cu_2S , with $E_g = 1.2 \text{ eV}$, and other semiconductor parameters as for silicon.
 - (ii) For CdTe cells, $E_g = 1.45$ was used, since the device appears to behave as a p-n homojunction in the base CdTe (See discussion below), and $\mu_n = 300 \text{ cm}^2 (\text{V} \cdot \text{s})^{-1}$, $\mu_p = 30 \text{ cm}^2 (\text{V} \cdot \text{s})^{-1}$, minority carrier lifetime 10^{-8} s .
 - (iii) For GaAs cells, $E_g = 1.35 \text{ eV}$ was used, as appropriate to the base material, with $\mu_n = 3000 \text{ cm}^2 (\text{V} \cdot \text{s})^{-1}$, $\mu_p = 600 \text{ cm}^2 (\text{V} \cdot \text{s})^{-1}$, and minority carrier lifetime 10^{-8} s .

The results of the calculations were rounded to the nearest order of magnitude, since the assumptions employed here do not justify higher accuracy. It was

assumed that the J_0 values for the junctions in these cells were roughly the same as those of homojunctions in the material with the bandgap used. This is a gross assumption. This assumption is the major contributor to the uncertainty of the end result, and this loss of accuracy arises directly from the present state of junction theory for these devices. It is interesting to find that if J_0 for the CdTe cells is calculated with the assumption that V_{OC} will be limited by the $E_g = 1.04$ eV bandgap of the Cu_2Te , then theoretical values of J_0 and V_{OC} are obtained which are surpassed by the actual measured values. This may be taken as supporting evidence for the opinion that the CdTe cells operate either as CdTe homojunctions or metal/CdTe barrier junctions.

- b. J_{SC} was calculated by numerical integration of Johnson's AMO sunlight spectrum over the range of energies greater than the bandgap of the material assumed to determine the spectral response of the cells, using response edges rounded for convenience in integration, as shown in Table XIII (526). It may be noted that the calculation procedure up to this point is essentially that used by Loferski (185), but the treatments differ with regard to the spectral distribution used, and hence there are small differences between the numerical results. This calculation of J_{SC} assumes:

- (i) zero optical reflection at the cell surface.
- (ii) no loss of photons by absorption in grids or barrier layer.
- (iii) 100% collection efficiency for photo-generated minority carriers.

These assumptions are of course not met in practice, but in the ideal cell these losses are absent.

- c. V_{OC} was calculated from J_0 and J_{SC} using equation (133), it being assumed that in principle a cell can be made with $A = 1$ in the diode equation.
- d. F was calculated numerically from the resulting I-V curve, it being assumed that the ideal cell has $R_s = 0$.
- e. η was calculated from V_{OC} , J_{SC} and F .

TABLE XIII. SPECTRAL RESPONSE FOR THIN-FILM CELLS

Base Material	Cut-off Material	Response Edge (Å)
CdS	Cu_2S	10,500
CdTe	CdTe	8,250
GaAs	GaAs	8,750

Table XII also provides a comparison between theory and experiment, the performance of the operating parameters in the best experimental cell being expressed as fractions of their theoretical values.

It will be recognized that the calculation procedures employed here provide only a rough estimate of the potential cell efficiencies. However, it is believed that this allows useful comparisons between the cells to be made.

Table XII indicates that no single parameter dominates the efficiency losses of any of the cells. Further, it will be seen that the CdS cell outperforms (on a relative basis) the CdTe cell in all respects, and the CdTe cell outperforms the GaAs cell similarly. For the CdS cell, the data indicate that F has probably reached the point where further advances will be hard to achieve, whereas improvements in J_{SC} and V_{OC} may be more easily obtained. However, this would assume that this cell's method of operation does not preclude the possibility of reducing J_0 and increasing J_{SC} : further progress in investigations of the mechanism of the CdS cell would be of great help in casting light on this question, a point which is taken up below. The same remarks regarding the attainment of improved V_{OC} and J_{SC} values apply to the CdTe cell, though in this case it may be more realistic to suppose that F can also be improved.

For the GaAs cell, the situation is very different, however. Measurements on real cells showed that the poor relative performance of J_{SC} could be accounted for very largely by surface reflection (20% of photons reflected) and by absorption in the surface barrier layer (30% of photons absorbed). This gives a collection efficiency for the remaining photons which is comparatively high. Table XIV shows a "balance sheet" for J_{SC} in the GaAs thin-film cell.

TABLE XIV. EFFECT OF LOSS PROCESSES ON J_{SC} FOR GaAs THIN-FILM CELLS

Parameter	Theory	Real Cell
Theoretical I_{SC} ($\text{mA} \cdot \text{cm}^{-2}$)	41	41
Absorbance of surface	1.0	0.80
Transmittance of barrier film	1.0	0.70
Transmittance of grid	1.0	0.95
Collection efficiency	1.0	0.95
Realized I_{SC} ($\text{mA} \cdot \text{cm}^{-2}$)	41	21

This points up the great advantage inherent in the ability of the CdS cell to use the photons absorbed in the barrier layer to generate cell output (assuming the basis of the 1067 model to be correct). The comparatively low value of F for the GaAs cell probably reflects the degrading effect of R_s . One notes that this would be likely to get worse in larger cells, and it should be pointed out that the areas of the experimental cells on which Table XII is based were very different (0.7 cm^2 for the GaAs cell, 1.8 cm^2 for the CdTe cell, 12 cm^2 for the CdS cell).

This brings us to a final point of comparison between the various thin-film cells. Taking the power available from a single device as a basis for measuring the state of development of the cell type, Figure 93 has been prepared. The ordinate displays (power available under $100 \text{ mW} \cdot \text{cm}^{-2}$ sunlight) as a function of (development time) in years on a logarithmic scale. The curve for silicon cells has been inserted for reference: it includes the development of dendritic cells. The starting point of research on some cell types is somewhat arbitrary: the dates chosen have been indicated, and the reader may feel inclined to modify the curves shown to fit his predilections. It will be noted that initial work on the CdS thin-film cell was done much earlier (1954) than the starting-date indicated on the figure. This cell type was quite different from that in use today, and hence this "false start" has not been indicated on the CdS development curve. The GaAs work may well represent a similar "false start", but this can not be proved or disproved at the present time. A conclusion which can be drawn, however, is that further work on GaAs thin-film cells should not be pursued unless a quite different approach is taken. Possibilities along these lines are discussed below.

It should be noted, however, that Figure 93 is strongly influenced by the fact that the data presented for most of the curves is taken from work on experimental cells, and the progress is determined to a large degree by increases in cell area. Although it has been found possible, in thin-film cells work, to trade off area against efficiency, the picture presented in the figure may be considered to be biased by the choice of experimental cells. For this reason, the dashed curve for production type silicon cells has been included, for reference purposes. One may wonder whether the accent on large areas in thin-film cells has in fact been premature, and that more emphasis on efficiency would have been useful, in view of this comparison.

2. Cadmium Sulfide

Research on CdS cells is unique in thin-film cell research in that there have been most of the time at least two groups at different laboratories working in the field. This has led to a competitive atmosphere, and one might be tempted to ascribe the comparative success which has been achieved to this factor. However, the relationship is probably more akin to the proverbial "chicken and egg" situation, since one might also expect more groups to enter a more promising appearing area of research. Nevertheless,

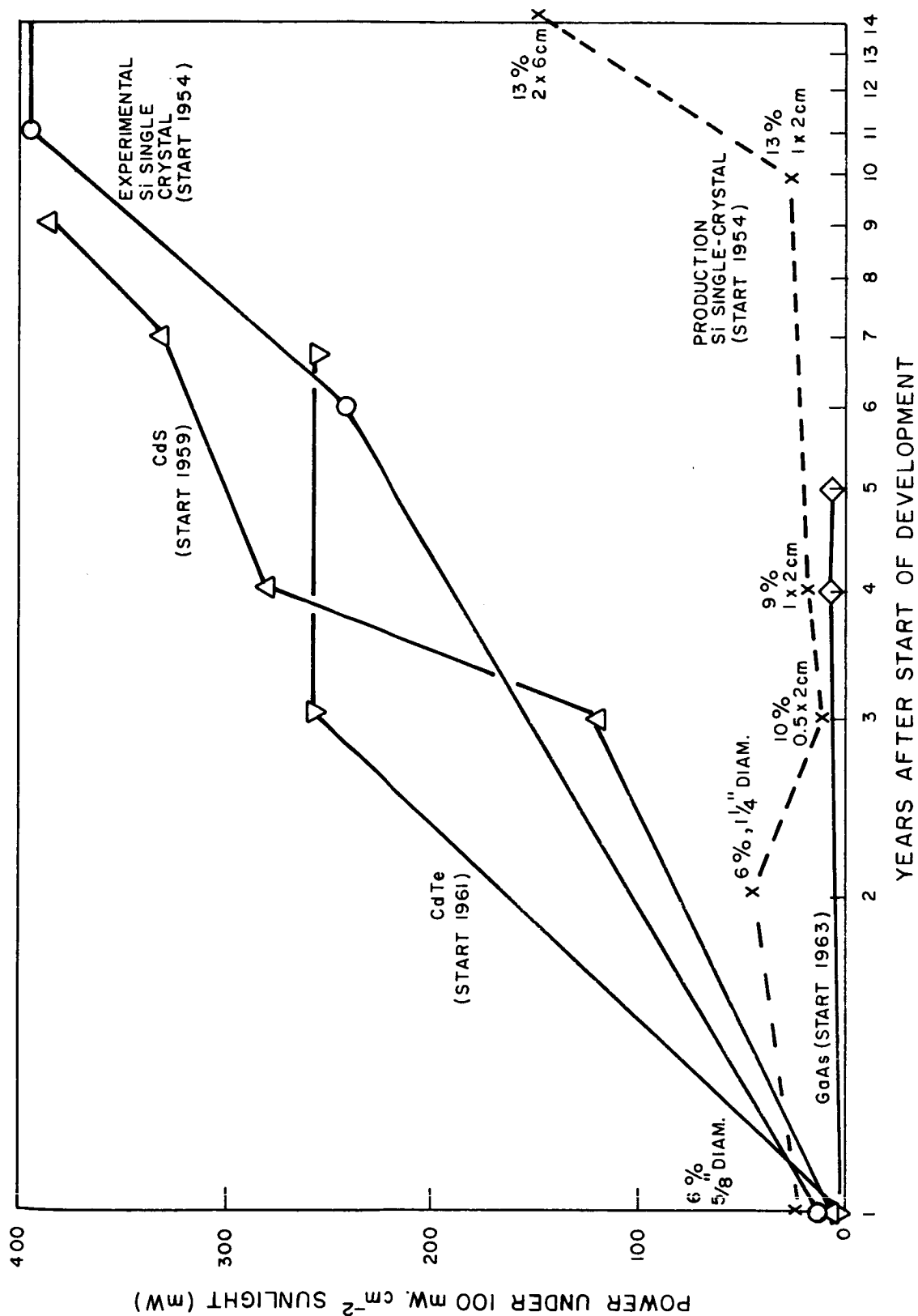


Figure 93. Graph comparing rates of progress in the development of various thin-film cell types, showing (power output per device) as a function of development time.

it seems that the comparatively rapid rate of innovation which characterized work during the 1961-1965 period may have been due to the desire to beat or meet the competition by introducing changes aimed at making a device which would be more acceptable to the user.

A good example of this is the use of plastic substrates. These were difficult to work with and gave poor results initially, and it would have been much easier to continue the use of molybdenum substrates. However, the RCA group felt it was worth putting effort into obtaining special plastics and demonstrating the feasibility of the concept. The Clevite group found it had to pursue the more difficult path also, and by perseverance both groups finally succeeded in making cells on plastic substrates with efficiencies almost as high as those on molybdenum.

It is also interesting to consider the speed of dissemination of information despite efforts aimed at preventing competitors from learning about new processes. The rapidity with which know-how of the dip process for making barriers spread, is a good example of such dissemination, together with the very common mode of travel: personnel transfer. Thus, the conclusion forces itself to the surface that, particularly where work is sponsored by government agencies, research results might just as well be fully reported, thus properly fulfilling the obligations accepted together with the public's money for research.

On the other hand, it is clear that the good progress which has been achieved on the CdS cells, is due in good part to the support which has been given to the research by the companies involved. All of the groups which have been involved in this work, at Clevite, Harshaw, NCR, and RCA, have received considerable support from company funds, and the government work has certainly benefited from this. Examples are the use of plastic substrates (developed by RCA on internal funding), and the invention of the dip process (originally discovered by Cusano at General Electric in the course of research on phosphors).

In looking at the alternative paths which the various groups have chosen to follow, several points appear worthy of discussion.

During the period 1965-present, the Harshaw and Clevite groups have used different methods for providing collector grids. The Clevite group has selected to continue using electroformed grids attached with various adhesives, whereas the Harshaw group has used grids deposited by electroplating through apertures in photo-resist masks. The Clevite group has achieved considerably higher conversion efficiencies, from which it might be implied that the Harshaw approach was unsuccessful. However, the reason for investigating electroplated grids was the stability problem which is at least partly connected with the use of the pressure- or adhesive-attached electroformed grids. Although progress has been made in reducing this problem, it has not yet been alleviated, and the Harshaw approach may still prove to be superior. In considering the likelihood of this happening, one observes that the plating process by

its very nature might be expected to be difficult to apply to the CdS cell, for the following reason. The cell structure is such that the plating current must cross the cell active junction. The current density for normal plating practice ($1 - \text{A} \cdot \text{cm}^{-2}$) is much higher than that at which the Harshaw group saw long-term changes in the cell I-V characteristic ($0.1 \text{ A} \cdot \text{cm}^{-2}$), and degradation of the cell characteristic by this process is a distinct possibility. (If the cell were an n/p device, instead of p/n, the junction would be reverse biased during plating: one has to be thankful that the cells are of the polarity they are.) Thus, some compromise had to be made between plating process requirements and cell degradation during the grid application, and this may be related to the present difficulties with the efficiencies of cells made with electro-deposited grids.

There exists a third alternative for grid formation: vacuum deposition. All of the groups involved in CdS cell research have tried to use this method at one time or another, and all have found that the process can lead to low efficiency cells, because of leakage across the junction. The fact remains, however, that this method is much more practical as a production process than the use of electroformed grids attached with adhesive, and in addition holds the promise of providing stability without the junction degradation associated with the plating process. One cannot help feeling that determination of the type shown in developing the use of plastic substrates might also lead to positive results in the development of vacuum-deposited grids. A point worth bearing in mind is that there exists a very wide range of variables in the vacuum deposition process, including material, evaporation source, deposition rate, and substrate temperature. This wide variety of possibilities increases the chances of finding a workable process, and recent results from the RCA work on vacuum-deposited grids indicate that progress is possible in this direction.

Both Clevite and Harshaw have used the cuprous ion dip process as their "standard" technique for forming the active junction since 1964. This method was a considerable advance over earlier processes, and although alternatives have been sought more recently, they have in no case given better results than the original process. One alternative has given very encouraging results, however, and further investigation of this appears justified. This method involves the use of organic solutions for the dip process, and was originally used by the RCA group during early work, and has been more recently investigated by the Harshaw group during 1967. The number of possible processing variations is large, and the elimination of water from the processing cycle may be valuable in improving stability.

It would be desirable to eliminate "wet" processing steps from the CdS thin-film cells manufacturing method, to allow all cell fabrication steps to be performed in one environment (e.g., vacuum), thus allowing semi-automatic processing schedules to be developed. The chemiplating process has given notably more efficient cells than such methods as vacuum deposition of Cu_2S or metal barrier layers onto the CdS surface, and it is interesting to speculate on the reasons for this. The Clevite and Harshaw

groups have studied the growth process of Cu_2S on CdS , and it appears from their evidence that in the region of the interface between the CdS and the Cu_2S , the crystal structure is essentially continuous. The junction is probably not abrupt, a progressive change in composition from the copper-rich surface to the cadmium-rich bulk material taking place. This may be a major reason for the high collection efficiency for the minority carriers generated on either side of the junction: if an abrupt junction were present, interface states would be expected to form which could act as recombination centers, leading to a reduction in collection efficiency, and possibly to poor diode characteristics based on the mechanism discussed by Shockley (see Section IV-A-1 above). The solution growth process can be expected to operate close to equilibrium, so that the resultant Cu_2S growth provides material which is near to crystallographic perfection. This situation is analogous to experience with thin-film deposition systems from vacuum or from the vapor phase: the nearer the growth process is to equilibrium, the more possible it is for atoms which are deposited in a crystallographically unfavorable location to either move to a better (lower potential energy) location, or to leave the substrate again. One notes that although slow growth is a necessary condition, it is not sufficient. To achieve similar equilibrium conditions in vacuum deposition would require higher substrate temperatures. At these temperatures, however, interdiffusion of the constituents of both substrate and deposited material takes place, leading to side effects in the resultant structure. These do not arise from the low temperature chemical deposition process. It has to be concluded that it will probably be difficult to find a better alternative to the dip process for making the active junction in CdS thin-film cells, although development of such an alternative would be desirable.

The question of the stability of the CdS thin-film cells has been one of the major problems from the earliest work. Initially, it was believed that the observed degradation was due wholly to moisture affecting the CdS junction, and that suitable encapsulation would eliminate this. Although encapsulants have been developed which largely alleviate the problem, the results are still variable. In addition, vacuum-thermal cycling has been found to lead to degradation by causing loss of adhesion between the grid and the barrier layer. Again, suitable choice of adhesive and grid material has been found to reduce the problem. However, despite considerable effort on this aspect over several years, elimination of the degradation problem does not appear near. Past experience indicates the value of independent testing of cells for degradation, the data produced by NASA-Lewis, Boeing, and Lincoln Laboratory (434, 435) being more revealing than those produced by the cell manufacturers. What has been tried in the recent past was the production of sufficient numbers of cells with tightly controlled manufacturing processes (to eliminate the variability seen previously with degradation measurements), to allow statistically significant numbers of cells to be life-tested. These engineering data must, however, be supplemented with research into the causes of the degradation: there has recently been a noticeable move in this direction with the establishment of Shiozawa's work at Clevite. Past experience has also shown that by the time the necessarily time-consuming degradation testing has been completed, the cell processing or structure has been changed, so that stability data have never been available for the current cell type. This situation must change before the cells can find application in space vehicles. In concluding this discussion of the stability problem in CdS thin-film cells, one notes that experimental results have established that

Hill and Keramidas' fear that all the cells may be inherently unstable is in fact ungrounded. However, their proposal that ion motion plays a part in cell degradation when it does occur is not disproved. Since such motion accounts satisfactorily for many of the observations on CdS cells, further examination of this point would be valuable.

Particle radiation testing has established that the CdS cell shows good radiation resistance compared to 10 Ω -cm n/p silicon cells: this result is as expected, and further discussion does not seem worthwhile. However, UV radiation testing has produced more worrisome results. It has been well established that the presently used Mylar lamination darkens rapidly under orbital conditions, to degrade cell output to near zero values within less than a year. The only solution found to this problem so far has been to substitute Kapton for Mylar, but this has resulted in a reduction of cell output by 20-25% because the Kapton absorbs an appreciable proportion of photons in the spectral sensitivity range of the cell. Spakowski has proposed the use of a thin Kapton coating to act as a UV shield on regular Mylar-encapsulated cells. However, results obtained with this type of construction have not been forthcoming. The Clevite group has reported that it is evaluating alternative encapsulants to solve the UV problem. Since delivered cells with Kapton encapsulation have shown efficiencies of only about 4%, which would be almost certainly too low for space application, it appears that the future of CdS cells depends on solving this problem, too.

The present mylar-encapsulated cells show efficiencies in the 5-6% interval. This appears to be marginal from the point of view of space application, since although the power to weight ratio is good ($> 100 \text{ W-lb}^{-1}$), the power per unit area is less than one half of that of silicon cells. This leads to problems in array design, for the reasons outlined in the introduction to this section. The presently used manufacturing processes appear, however, not to be the same which gave the most efficient cells in the laboratory. The reason for the selection of the present process seems to be difficulty experienced in achieving control in the other processes, so that more reproducible results could be obtained by using the process which leads to lower-efficiency cells. Therefore it appears that, although increase of efficiency is not the most critical item at this time, work aimed at obtaining control of the high-efficiency processing methods would be worthwhile.

It is also for the objective of efficiency improvement that research on the cell mechanism is necessary. In the first place, an understanding of the device operation will outline the areas in which efforts at improvement of the conversion efficiency can be most fruitful. This is illustrated by the improvements in silicon cells achieved through the provision of grids, through making the diffused layer as thin as possible, and through the provision of antireflection coatings: each of these areas for improvement was pinpointed by comparison between experimental measurements and theory. Secondly, an understanding of the cells should lead to an estimate for the ultimate efficiency of the CdS cell, which would in turn indicate how much effort it would be worth putting into attempts to improve efficiency. It is for this reason that the recent work of Shiozawa's group at

Clevite, and of Potter at NASA-Lewis, is considered to be the most significant advance in several years in the thin-film CdS cells field. This has provided, so far, the closest model of cell operation, and further research will be of major importance to fill in the details of the energy band structure, and to relate this structure to the cell manufacturing processes.

There is a point at which the 1067 model, and the explanations of its operation given by Shiozawa and by Potter, appears to require closer examination. Data given by both Potter and Shiozawa show that the effect of green bias light on the cells is to increase the spectral sensitivity in the red region of the spectrum. Both explain the effect in terms of photoconductivity induced in the intrinsic CdS layer by the green light. Such photoconductivity undoubtedly occurs, as is evidenced by the measured decrease of series resistance under illumination. However, the illumination levels in the monochromators used for measuring spectral response are much too low for the I_{SC} to be series-resistance limited during such measurements. Rather, the increase in I_{SC} caused by green bias light must arise from an increase in collection efficiency. In fact, the 1067 model as proposed by Shiozawa provides a mechanism for this. Referring to the band structure as shown in Figure 73b, it will be seen that the change in conduction band shape in the intrinsic region under green light illumination is such that motion of the electrons through this region will be field-assisted. This will decrease the transit time of the electron through this region, leading to a reduction in the probability of recombination. This explanation of the effect of green bias light can also be taken as evidence supporting the difference between the 1066 and 1067 models, since the 1066 model would not produce a major effect of this nature.

This leads to the final point to be discussed with respect to CdS cell evaluation. Comparisons between CdS cells and silicon cells indicate that the area where the CdS cell can compete most effectively is in cost per unit power output. At the present price of \$15 per cell, this is approximately \$45 W^{-1} , compared to the silicon cell cost of \$60-\$80 W^{-1} . It seems that the price of the CdS cells would have to come down a good deal further to offset the extra cost of array structure and deployment mechanism needed for the larger CdS array, compared to a silicon array of equal generating capacity.

A much larger cost reduction would be needed for CdS film cells to find significant terrestrial application. The present situation with regard to comparative costs of solar and conventional electrical power generation for terrestrial application was reviewed by Wolf (527) and by Duffie and Lof (528). It was shown that if cell costs could be reduced to \$10 W^{-1} , photovoltaic power would be competitive for small remote-location use, but that cell costs of \$1 W^{-1} would be needed for direct competition with conventional power in normal industrial or domestic use in developed countries. This realistic cost requirement necessitates that CdS cells be manufactured by automated mass production systems which are unlikely to be developed in the foreseeable future. This also implies that, during this period, the costs for space cells will not decrease significantly because of increased production for terrestrial applications. There are some points to be made which may overrule such exclusive cost considerations, however:

- a. thermal pollution from fossil fuel or nuclear generating stations is already a problem, and will increase proportionately with power generation in the future. Photovoltaic systems cause no thermal pollution.
- b. certain loads, notably airconditioning, are particularly suited to operation by solar power sources, not requiring power storage.

In view of these considerations, it would appear unwise to rely, for cost reductions, on commercial sources to provide funds for research purposes or developing large volume manufacturing processes for large-scale terrestrial application of CdS solar cells.

Aside from processing variations, one further method is available for the reduction of array cost. One half of the price of an array arises from the assembly and interconnection processing needed. An appreciable cost saving could therefore be made by reducing the assembly steps needed to go from cells to arrays. This could be achieved either (a) by increasing individual cell areas, or (b) by making cells already connected into submodules by the cell fabrication processes. The 55 cm² Clevite cell is a move in the first direction, and the group is reportedly working on still larger cell areas (100 cm² and greater). There is no doubt that the cells presently made by Clevite provide a major step towards array cost reduction, but there is a limit to the amount of progress which can be made in this way. The 55 cm² cells produce currents close to 1A, and reducing cell series resistance to a sufficiently low value is already a problem which has been solved only with difficulty. Although cell areas could be increased by making larger cells in a geometry which essentially puts smaller cells in parallel, the series resistance problem still exists, being then concentrated in the interconnections. Also, array reliability could then become questionable because a single short-circuit could prevent output being obtained from an appreciable portion of the array. A way around this problem is contained in the second approach, using a cell fabrication technique which allows the formation of submodules of series-connected strings of cells during cell fabrication. Output from a series-connected string would be lost if an open-circuit occurred in one cell, but experience shows that with CdS thin-film cells this is much less likely than the development of short-circuits. The series-connected integrated array would therefore provide a more reliable format than a parallel-connected array (or its equivalent as a single cell), and by the same token, a higher production line yield should be obtained.

At RCA, a group under Hui has been working towards this objective, but full success in achieving the desired result of semi-automated processing would involve developing barrier-formation and grid-formation processes which are based on vacuum depositions. Although versions of such integrated arrays have been made at RCA with processes similar to those used at Clevite, achievement of the ultimate cost savings can not be expected from this method because of the need to remove the submodules from vacuum to apply the dip process for making barriers, followed by manual application of the collector grids. In principle, these processes could also be automated, but with greater

difficulty and probably at the expense of longer cell processing time. Besides, experience has shown that for the cell quantities needed for space power systems, hand operations are still cheaper, since the required mechanization processes are neither simple nor of low cost.

If all fabrication could be done by semi-automatic processing in a single vacuum system with multiple evaporation sources, these conditions would be more readily met. To realize this, successful development of vacuum processes to replace the barrier-formation dip process and the manual grid application will be needed. However, the potential of the concept is great, and makes it attractive as a longer-term development project.

One omission has been noted in reports of CdS processing, and its absence provokes thought. Almost all etching processes are to some degree electrolytic in nature, and the ion exchange reaction used to form the Cu_2S barrier almost certainly involves electrical surface activity. In view of the marked effects which illumination has on the electrical properties of CdS, it seems remarkable that the effect of light on the barrier formation process, or the etches associated with this, should not have been examined.

In conclusion, it is observed that the work on CdS thin-film solar cells has been one of the most promising fields in photovoltaics development for some years, but that the empirical attempts to improve the cells of the past must give way to more direct research towards understanding cell operation and degradation mechanisms if good progress is to be obtained in the future.

3. Cadmium Telluride

In contrast with the CdS thin-film cell work, CdTe has not elicited widespread interest for solar cell research, the GE group originally under Cusano having been almost alone in the field since the inception of work in 1960. Good progress was maintained during the early phases, this early work possibly being aided in part by techniques developed by Cusano during investigations of phosphors and other semiconductors during the late 1950's.

Of all the proposals which have been made for thin-film cell types, the CdTe cell probably makes the strongest case on paper:

- a. The bandgap is close to optimum for matching to sunlight, thus providing high theoretical efficiency.
- b. The material is a "direct" semiconductor, thus allowing a device to be made from a very thin layer of CdTe.
- c. Thin films can be made both n- and p-type with reasonable semiconductor properties.

The early work, during 1960, was directed towards establishing these fundamental points, and the results gave a logical justification for pursuing the development of the cells.

This groundwork laid, attention was focused on developing CdTe layer formation methods. This was again a logical step, which was pursued in the right direction, that is towards layers being formed from the elements. Such a process should result in much lower manufacturing costs than one which uses the compound as the starting material. Add to this the fact that the equipment used for the CdTe layer growth did not require ultra-high vacuum or an ultra-clean working environment, and one can conclude that this early situation looked very promising indeed.

The use of the molybdenum substrate during the early work was justified. The material has the required metallurgical properties, in that it allows high-temperature processing, and is resistant to attack by the other materials used in cell fabrication. Its coefficient of thermal expansion matches that of CdTe reasonably well, thus minimizing problems such as delamination of CdTe from the substrate, and curling and cracking of the Mo/CdTe composite. In addition, it is readily available in the required thin foil form, and is more easily handled than many foils because of its high strength and elasticity (cf. aluminum or copper, which wrinkle and crease easily when in thin foil form). However, molybdenum foil is expensive (comparable with or higher in cost than silver foil), and is heavy, with a density of 10.2 (cf. Al, density 2.6). Although recent work has enabled the foil to be thinned by etching after cell formation, to give very thin substrates providing higher power-to-weight ratios, the application of such a technique on a production scale could be costly.

Recognizing this fact, the GE group has recently re-opened the question of alternative substrate materials. It is unfortunate that the processing temperatures needed for the formation of reasonably crystalline CdTe layers (400 - 450°C), are beyond the range over which the present high-temperature plastics (e.g., the polyimides used in the CdS cells work) could be used. Progress toward the use of plastic substrates has to await the successful outcome of research at one of the chemical companies, where research on high-temperature plastics is proceeding, unless a lower-temperature deposition process for CdTe can be developed in the meantime. Under these circumstances, the decision to try to use a lighter metal, such as aluminum, for the substrates, appears reasonable. Although the GE group has not stated explicitly why cells on aluminum substrates have shown low efficiencies, it may be assumed that the Al/CdTe interface provides a high-resistance or even non-ohmic contact. This problem was also met with molybdenum substrates, but a solution was found. Although the same solution, the use of a CdS intermediate layer, may not be applicable to the aluminum substrate, there are plenty of alternatives available: the In_2Te_3 used by the Harshaw group to give low Mo/CdTe contact resistance might be a useful start. It appears that efforts to overcome the difficulties which have been encountered in this area are especially worthwhile, and should be continued with determination.

Returning to the early GE work, the final point to be discussed is the barrier formation process. The CuCl dip method, used since the very earliest stages, has been found to be a practical method for making the active junction, and good process control has been achieved.

Perhaps more significantly, the use of a graded-conductivity CdTe surface layer to improve cell efficiency was also initiated. The action of this surface layer, in providing a field which aids in minority carrier collection throughout the region where most photons are absorbed, is well understood, and provides further theoretical support for the belief that the CdTe thin-film cell should be a viable device. The development of methods for controlling the thickness of this layer, during 1962 and later, and for obtaining an adequately uniform field, is one of the major achievements of the GE work. Comparable process control in the formation of vapor-grown layers of silicon or gallium arsenide has been achieved only with great difficulty, involving a much greater research effort which has been pursued widely in the electronics industry. The ability to achieve such process control in the deposition of CdTe layers is a further practical reason for feeling that research on CdTe thin-film cells is worthwhile.

The successful replacement of the electroformed metal mesh collector electrode by a vacuum-deposited gold grid structure, during the 1962-1964 period, was a highly desirable development, in view of both cost and reliability, by providing a process more suited to production-scale methods, and by avoiding difficulties such as have arisen in the CdS cells with separate meshes attached with adhesive. However, the vacuum evaporation process limits the thickness which can be achieved in the grid lines to about 1-2 μm , since thicker layers tend to peel from the substrate. This is a general phenomenon, and arises because vacuum-deposited layers contain built-in stresses. These stresses are separate from effects caused by differential thermal expansion, and appear to arise from the crystal growth processes occurring during film formation. Although the use of special alloys, or of multi-layers of different materials in which compressive and tensile stresses alternate and hence cancel each other, can avoid the problem, these solutions are expensive and may be difficult to make compatible with other constraints on the system. The GE group has borne the limitations in grid layer thickness in mind throughout their work, and this consideration determined the choice of the present cell geometry, a 4" x 1" cell with a busbar along the long dimension, thus keeping the conduction path length in the grid lines within reasonable bounds.

Up to 1964, good progress was achieved, with a fair rate of innovation and improvement of cell efficiency and area, from the 1962 figure of 6% for a cell of less than 1 cm^2 , to the 1964 figure of 4.6% (maximum) and an area of over 50 cm^2 . During 1965, however, the move towards pilot-line production started. Perhaps because the CdTe cell was competing with the CdS cell, when the latter moved to pilot production, the CdTe work was also pressed in this direction. The present situation seems to indicate, however, that entering the pilot production phase with thin-film CdTe cells was premature. In

the succeeding period, innovation has been less noticeable, and cell efficiencies have not improved. This would not be important if the average efficiencies of pilot line cells were higher, perhaps 5%. While an initial drop in yield and product performance upon transfer to pilot-production is to be expected, due to the learning curve of personnel involved, sufficient recovery has not been achieved, even after a period of several years. Whether this is due to too great a difference in personnel and approach of the production group, to insufficient communication between the research and production groups, or to over-selling of the research cells, will not be really possible to determine. Taking the move toward pilot-line operation as a fact, however, a constructive look at the present situation is in order.

Two fundamental problems face the CdTe cells today: efficiency and stability. The efficiency of cells must be at least 5% before consideration of application becomes possible, and 8% or more before it becomes probable. Assuming that research-type cells have actually been made with efficiencies in this range (there might have been a measurements problem), optimism should be indicated. The problem then would simply be one of establishing reproducible processes corresponding to those on the research cells. This may not be an easy task: for silicon solar cells, it has taken about 5 years, with substantial production going and many man years of effort. In any case, the pilot line effort should be augmented with substantial research to illuminate and understand the problems encountered. The current work aimed at developing methods for obtaining more uniform CdTe layers is undoubtedly of value here, but taken alone is not enough.

Completely different approaches are also not to be overlooked. Research results with AgNO_3 -treated substrates, which provided patchy results, but some very good cells during 1965, indicate another possible line of attack. The mechanisms underlying the effect of various substrate treatments on the cells could also be a fruitful field of investigation. A different approach to barrier formation processes could also be profitable, especially in view of the French results with vacuum-deposited Cu_2Te layers. Although the efficiencies seen with junctions formed by this process have not so far been as high as those with the dip-formed barriers, the results indicate considerable potential. In addition, a vacuum-deposition process would have advantages for manufacturing, in potentially allowing CdTe deposition, barrier formation, and grid application, to be performed on a semi-continuous schedule. Re-investigation of the type of dopant used to form the graded carrier concentration in the surface region also appears to be potentially fruitful although the GE group has already done considerable work in this area. The hoped-for improvement in cell efficiency could arise from the elimination of copper from the CdTe, since this dopant not only provides the necessary donor levels, but probably also has deeper energy levels in the forbidden band, which can act as recombination centers. As long as the Cu_2Te barrier layers continue to be used with processing schedules which include significant heating, so that diffusion of copper into the CdTe can take place, it seems unlikely that advances from elimination of copper doping in the rest of the cell could be realized.

The fact remains that CdTe ought in principle to yield good solar cells, and the experimental work which has been done shows that the technology is easier to handle than that of many other semiconductor materials.

Efficiency and stability might be simultaneously obtained from further attention to the anti-reflection coating methods. Again, this is a field which has received wide study in the past. Experience both here and in the CdS work definitely indicates that plastic encapsulants provide much better protection from moisture degradation than do inorganic coating materials, although this is in contrast to experience with silicon devices. Good results were obtained with alumina (Al_2O_3) as regards anti-reflection effects, but assured stabilization against moisture degradation was not forthcoming. Up to this point, experience indicates organic coatings to be more likely to produce good stability. It appears that more investigations of such organic materials for the CdTe cells are needed. A potentially fruitful approach may lie in evaluating the epoxy used in the CdS cell lamination process, since this appears to have proved effective in combating moisture penetration. (It is possible that this material has in fact already been evaluated by the GE group, but it is not possible to determine this from reports, since the epoxy has not been identified by the Clevite group.) Just as for the CdS cells, it appears that research into the details of the degradation problem could also do much to guide the present largely empirical attempts to provide cell stability.

In summary, then, it must be stated that the present situation in thin-film CdTe cell research appears disappointing in view of the early promise of this device. However, the introduction of a lightweight substrate, together with the achievement of efficiencies in production cells comparable with those seen in research, could enable these devices to provide the CdS cells with some stiff competition. It should also not be overlooked that total research and development funding spent on CdTe as a material, as a semiconducting device, and as a solar cell, is very much smaller than that spent on CdS.

4. Gallium Arsenide

On superficial observation, the situation of the GaAs thin-film solar cells looks very similar to that of the CdTe device. Closer scrutiny, however, reveals some fundamental differences. The RCA work on thin-film GaAs cells has been virtually the total effort in this field, the French interest having disappeared rapidly when the problems of obtaining good semiconduction properties in GaAs films became apparent. Of course, the other thin-film cell types (CdS and CdTe), provided a competitive stimulus.

The theoretical advantages of GaAs as a thin-film solar cell material (good bandgap match to sunlight, and "direct" optical absorption) were well established before work on the cells began. From the start, therefore, the work was aimed at solving practical problems. These mainly centered on the technological difficulties of working with GaAs, including:

- a. the high temperatures necessary for film growth ($\sim 700\text{--}800^\circ\text{C}$, compared to $300\text{--}400^\circ\text{C}$ for CdS, and $400\text{--}500^\circ\text{C}$ for CdTe).
- b. making thin layers with reasonably low resistivity and high carrier mobility and lifetime.
- c. making low-resistance ohmic contacts to the material.

The first problem to be tackled during the early work was the development of methods for preparing thin layers of GaAs. The vapor-transport method settled on was certainly the best available at the time. However, the process requires high purity wafers of the compound as the starting material, which would have made it impractical for application on a production basis which includes maintenance of acceptable costs. However, the choice was justifiable for research purposes, it being reasonable to suppose that the general interest in developing methods of producing epitaxial GaAs would have pointed the way to a cost-effective process for making thin-film solar cells, by the time these reached the production stage. This expectation has already been partially justified, since excellent epitaxial GaAs growth methods are now available. There can be no doubt that the continued attempts throughout the duration of the work to develop better GaAs growth methods was an important aspect of thin-film cells development, and that even the negative results of most of these attempts contribute to the presently available stock of knowledge. However, there is accumulating experience that the technology of III-V compounds, including GaAs, is intrinsically more difficult than that of the elemental semiconductors and II-VI compounds. This will make the achievement of low-cost GaAs devices more difficult.

As for the CdS and CdTe cells, the choice of molybdenum as a substrate material was a reasonable one for research purposes, because of its metallurgical properties and its availability. Again, the intent was reasonable to substitute aluminum foil, a lower-density, lower-cost substrate material, at as early an opportunity as possible. Whether the actual attempt to do so was undertaken too early may be debated. Also, the particular choice of aluminum caused some processing problems, since its low melting point (660°C) limited the GaAs growth temperature, which in turn led to difficulty in obtaining good crystallinity and adequate electronic properties. Although adequate GaAs-layer crystal quality was eventually obtained, the material was never electronically good, as evidenced by the minority carrier diffusion length estimates made from collection efficiency and barrier width measurements. The limitations imposed by the substrate would probably prevent any substantial improvement in GaAs quality, provided the vapor transport deposition process was continued to be used. Investigation of alternative GaAs layer growth methods was therefore of importance to the substrate problem, too.

Since there can be no foreseeable expectation of developing a plastic substrate capable of withstanding the GaAs layer growth temperatures, the only alternatives are metal foils. None can compete with aluminum for low weight, low cost, and availability, but titanium might be a possibility in providing a compromise between aluminum and

molybdenum, with good high-temperature capability. An immediate difficulty with titanium is posed by its disintegration on heating in hydrogen, so that it could not withstand the GaAs layer growth ambient. The substitution of a noble gas for hydrogen in the furnace might be a possible approach to solving this problem.

The early work showed that the use of solid-state diffusion to form the active junction was not possible, because rapid diffusion along the grain boundaries led to leakage across the junctions. In spite of considerable improvements in the quality of the GaAs layers during the course of the work, this initial result was confirmed by later attempts to form diffused junctions. Although this is disappointing, it is in agreement with the experience of others with diffusion in polycrystalline materials, and was therefore not unexpected. The use of a heterojunction or barrier-layer type of cell must thus be considered the natural approach to a thin-film solar cell. The results of others in attempting to form heterojunctions using GaP on single-crystal GaAs base material indicated that the epitaxial growth of related III-V compounds with larger bandgaps was unlikely to yield good results, and the investigation of alternative metals and compounds covered a wide range of alternatives. The two possibilities which this search turned up, platinum and non-stoichiometric cuprous selenide $\text{Cu}_{1.8}\text{Se}$, provided what seem to be the best representatives for the two possible approaches using metal films for making barrier contacts, and p-type semiconductors for making either heterojunctions or, if highly degenerate, effectively barrier contacts. To pursue these two alternatives in competing projects was a reasonable move. As it turned out, the p-type semiconductor was degenerate to such a degree that the cell with this type of junction acted, in effect, also as a metal-barrier contact cell, so that the efficiency of the devices from both approaches depended on:

- a. the optical-transmission/series resistance combinations which could be achieved by the barrier contact film in conjunction with metallic contact grids: this in part determined the I_{SC} and fill factor obtainable, and
- b. the surface states which could be induced by a combination of etches and the surface barrier layer deposition process: this determined the V_{OC} .

Given the barrier layer material, the improvement of cell efficiency by the first-listed factor is a problem in optimization with two major variables (barrier layer thickness and grid line spacing), and this optimization process appears to have been investigated fairly thoroughly, though only by empirical means.

The second factor (the provision of a desirable surface condition) can only be investigated empirically at the moment. The situation reached quite early in the work was that barrier heights sufficient to give low efficiencies (3% or less) could be achieved reproducibly and without much difficulty, but the only method discovered for improving on this performance (post-barrier etching) led to unstable cells. In spite of an attempt to analyze this phenomenon, an understanding of its mechanism was

not achieved. Whether a more extended research effort into the effect would have had beneficial effects is an open question. The fact is that surface state effects are in general little understood, and a research effort adequate to give an understanding of the effects seen in the solar cells would be costly, particularly since the polycrystallinity of the semiconductor may well have complicated the situation considerably.

A further point is that a semiconductor surface which has been prepared with a special set of surface states to give a desired result is not only difficult to achieve reproducibly, but is also easily "poisoned" by reaction with its environment. It follows that the reproducible fabrication of cells needing a special surface condition would not only require very clean manufacturing facilities, which could be costly, but, more important, the stabilization of such cells against degradation could be difficult to achieve. This is not to say that efforts to make such cells have to be doomed to failure, since it might be that a barrier-forming material can be found which will provide both a stable condition and a high surface barrier.

In considering the decision to discontinue work on GaAs thin-film solar cells, it has to be concluded that this was the correct course to take in view of the problems facing the work. If, in the future, the technology of deposition methods for GaAs advances to the position where thin layers can be formed at reasonable cost over large areas ($\sim 50 \text{ cm}^2$ in place of the present $\sim 1 \text{ cm}^2$), this decision would be worth reconsidering.

In examining the work done by the French group in the area of GaAs thin-film cells, one can only regret that the difficulties in GaAs material preparation are so great as they are. The evidence produced by diverse groups has been consistent in demonstrating that vacuum-deposition techniques for forming thin films of GaAs do not produce material having useful semiconductor properties.

5. Other Materials

This section will deal with work on thin-film cells made of other materials. In addition, various materials shall be considered which are potential candidates for use in thin-film cells, but on which no work has been done.

Attempts to make thin-film cells using silicon were criticized on theoretical grounds right from the start. For the reasons described in Section IV-D-1, the optical properties of silicon are such that the cells must be made of several mils thickness if large losses in efficiency are not to occur. Since single-crystal silicon cells can now be made at reasonable cost with thicknesses minimal for reasonable efficiency, thin-film silicon cells offer no weight advantages. Although the growth of thin layers of polycrystalline material offers potential cost-saving advantages over the use of single-crystal wafers, considerable experience has now accumulated to show that these cost-savings are unlikely to be achieved in the near future. In addition, the polycrystallinity has been shown to lead to lower efficiencies by reducing minority

carrier diffusion length and by leading to non-uniform solid-state diffusion fronts in the junction-formation process. It is concluded that although an investigation of the potential cost savings of thin-film silicon cells was justified, further work in this area is unlikely to yield useful results.

One of the more promising cell materials, which has received a little attention, is cadmium selenide (CdSe). The energy bandgap of this material is 1.7 eV, rather higher than the optimum for solar energy conversion, but nevertheless giving an indicated theoretical efficiency of over 20%. Optical absorption measurements show a sharp rise in absorption constant for photons with energies greater than E_g , so that the material fulfills the fundamental requirements for thin-film cell use. The Harshaw group under Heyerdahl gave considerable attention to making thin-film cells of CdSe, and made appreciable progress in obtaining physically suitable configurations. However, the electrical quality of the cells was found to be inadequate, and it was concluded that the material always gave low V_{oc} values, for reasons unknown. Komashchenko and Fedorus of the USSR have recently reported results on single-crystal CdSe cells which show confirmation of this, having V_{oc} values of 300-350 mV (see Section IV-C-6), and yet having appreciable efficiencies (3%). It appears that an investigation of CdSe thin-film cells would be justifiable if other types of thin-film cell did not exist. There exists now no evidence to indicate that this cell would have significant advantages over the CdS or CdTe cells. Thus, in the context of the present situation, work in this area cannot be recommended.

In reviewing the work done in the US on CdSe thin-film cells, one will realize, with surprise, the close limitation of the effort. For instance, alternatives to the dip process for junction formation were not examined. The Russian work on single-crystal CdSe cells appears to have been more extensive. In particular, cells have been made with barrier layers of vacuum deposited metals and of cuprous selenide.

Two groups have taken a brief interest in $Cd_{1-x}Hg_xTe$ cells, one at GE Laboratories (under the CdTe thin-film cells work), and the other in France. Such work is difficult to justify on theoretical grounds, since the addition of HgTe to CdTe moves the bandgap value away from the theoretical optimum for solar energy conversion. The work could only be justified by hoping that, contrary to theoretical expectation, the J_{sc} increase caused by reducing the bandgap and moving the spectral response to longer wavelengths would not be offset completely by the loss in V_{oc} value which would also accompany a reduction in bandgap. The work shows that this hope is not fulfilled, so that further work could not be justified on practical or theoretical grounds.

Virtually no work has been reported on thin-film cells made of III-V compounds other than GaAs. Candidate materials with bandgaps in the right range for good solar energy conversion are aluminum antimonide (AlSb), gallium phosphide (GaP), and indium phosphide (InP). Results with both AlSb and GaP indicate that the technologies of these materials have special problems which make them unattractive for use in thin-film solar cells; for an account of these, see Section V-D. InP appears to provide fewer technological difficulties, although it is typical of a III-V compound in being more difficult

to deal with than the II-VI semiconductors. However, recent results with single-crystal cells prepared by Galavanov's group in Russia (see Section IV-C-3), in which conversion efficiencies up to 6.7% were seen, could be taken as encouragement for work on thin-film InP devices. However, there seems little doubt that any program aimed at developing such cells would be required to make heavy investments in developing the material technology of InP. It is, of course, an open question whether or not such investment would be worthwhile, but drawing on the experience of the GaAs work, one must conclude that there is no logical justification for a research program in this area.

One material remains which deserves brief discussion: selenium. Work on selenium photosensitive devices in thin-film form has been in progress since the last century, and it must be assumed that the technological aspects of this material have reached a state of maturity. Since the bandgap is not suited to solar energy conversion, there appears to be little reason to hope that cells can be made which are noticeably more efficient than the 1% value presently seen in photodetectors.

This concludes the evaluation of past research on thin-film solar cells. Suggestions for future, potentially fruitful, investigations, based on this evaluation will be found in Chapter VI of this report.

F. ADVANCED TOPICS

1. Organic Materials

The work which has been done on photoeffects in organic materials has established conclusively that these compounds are potentially capable of generating power by the photovoltaic effect. With the demonstration of this potentiality, work has been supported by the USAF, aimed at further examining the possibilities. This work has had two principle objectives:

- a. elucidating the electrical conduction and photosensitivity mechanisms in organic materials, and
- b. identifying specific compounds which can be employed in making useful devices.

For a summary of government-funded projects in this area, see Table XXI in Appendix III.

Although a great deal of work remains to be done, it appears that an understanding of the phenomena observed is being assembled, and that there are no theoretical reasons why organic semiconductors should not eventually be used as the basis of practical energy conversion devices. It remains, therefore, to find the right materials for the

job, hence item (b) above. An evaluation program which synthesises and purifies candidate compounds and measures their properties appears to be the right approach to this task. Using the guidelines of good electrical conductivity and photosensitivity, this search need not be wholly random, and this has been the approach followed by the various groups working in this field. Although a material really well suited to energy conversion has apparently not yet been found, the results which have been achieved indicate that progress is being made, and that it may be only a question of time before good cell efficiencies are obtained. The advocates of organic solar cells point out that the number of candidate compounds is so large that it seems certain that one with the necessary properties will be found.

There are various criteria aside from conversion efficiency which must be applied to evaluating possible solar cells, however. Many of these may be regarded as "second-generation" problem areas. However, one which we wish to emphasize in regard to organic cells is stability. It can be anticipated, in the light of past experience with organic materials such as dyes and plastics, that organic solar cells may be sensitive to both UV and particle radiation. The degradation caused by such irradiation can proceed by two mechanisms:

- a. chemical bonds are broken, so that molecules break down into their constituent groups, or
- b. chemical bonds are rearranged, often resulting in a polymerization reaction.

Polymerization is determined by the overall structure of the molecules involved, and is difficult to predict in advance. Breakdown of molecules should be easier to predict, since the bond strengths in a molecule can to a large degree be predicted in advance from measurements of the behavior of the same bond in other molecules. This is because the major factors determining bond strength are the groups immediately adjacent to a bond, and although other groups in the same region of the molecule can have an effect on the bond strength, this is generally small (a second-order perturbation), and can in any case be estimated in advance also. Hence, because of the "building-block" structure of organic molecules, a program of experimental measurements to determine the behavior under irradiation of samples of organic materials containing the groups and radicals used in making organic photovoltaic compounds, should permit prediction of the behavior under irradiation of new candidate materials. At the least, such a series of measurements should act as a guide to identifying possible compounds. It may even be found that no organic compound will be adequately stable under irradiation, and thus a needless expenditure of a large research effort on photovoltaics could be avoided. Note that this is not to say that all research efforts on organic semiconductors should be discontinued in the latter case: the potential value of semiconduction in organics extends over far wider fields than space power supplies.

The same research proposal covers both organic compounds intended for use as the base material in solar cells, and those which could be used for sensitization of inorganic base materials. As noted in the discussion of the multiple-transition solar

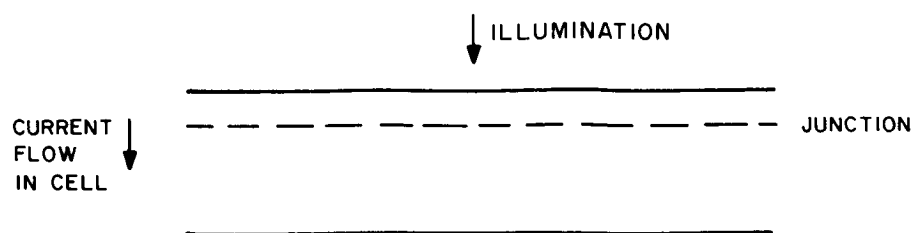
cell (see Section V-B-6 above), the sensitization process may be useful in providing one of the transitions in this type of cell. Such a possibility must be considered as unlikely to come to fruition for several years, however, even if the theoretical work on the multiple-transition cell indicates the feasibility of the device.

In examining the work which has been done on organic photoconductors, it is interesting to note a problem in communication which has arisen in this work. This has been caused by the multi-disciplinary nature of the research field, embracing both organic chemistry and solid-state electronics. Thus, for instance, Nelson's discussion of photovoltages developed between an organic layer and a CdS substrate appears to neglect the likelihood that almost any material deposited on CdS will develop a photovoltage under illumination, arising from the inversion layer at the CdS surface. With growing interest and increasing experience in this field, however, this type of problem should become less likely to arise. For instance, reports of photoeffects in organic materials have recently started to specify the type and intensity of illumination used in the experiments, a point conspicuously absent in most of the early reports.

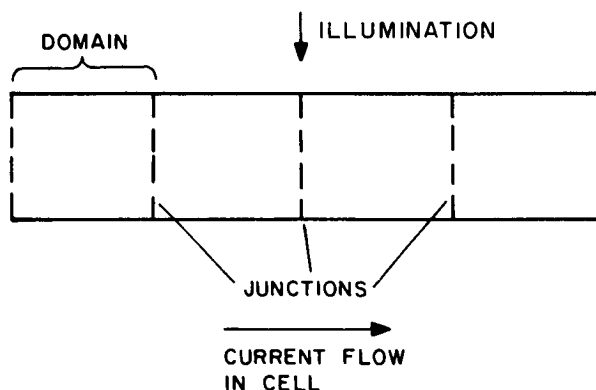
2. The High-Voltage Photovoltaic Effect

When this effect was first identified and investigated by the RCA Laboratories group during 1957, it appeared that it would prove to be very advantageous for use in power generation systems. As the original workers noted, however, practical application would require that the device internal impedance be reduced sufficiently that reasonable J_{SC} values could be achieved. When efforts to improve the efficiency of the devices, by searching for other semiconductors and by evaluating alternative fabrication techniques, failed to bring results, interest in this area quickly waned in the US. This was the logical reaction, under the circumstances, and nothing has occurred since to indicate that the cessation of work was premature. Indeed, the recent Russian results show that the expenditure of effort in this field would be most unlikely to be worthwhile, from the practical point of view. This calls into question the reasons underlying the considerable Soviet interest in this subject in recent years. One can only conclude that pure scientific interest in providing an explanation for a curious phenomenon has provided the motivation for this work.

In evaluating the potential of the effect for the generation of power, some observations may be made which indicate that practical exploitation of the phenomenon is unlikely. This is based on the fact that the device geometry is fundamentally different from that of the normal solar cell: see Figure 94. It will be observed that in the high-voltage device the illumination must fall on the edge of the active junction, and thus the photo-generated minority carrier density will be non-uniform across the active junction. In addition, the collection efficiency is not uniform over the surface of the device, on a scale comparable with the domain size. Thus, the cell structure cannot be optimized, and it appears that it will be difficult to obtain good J_{SC} values. These disadvantages can be minimized by use of material with long minority carrier diffusion lengths, but



a. Conventional cells.



b. High-voltage cells

Figure 94. Cross-sections of photovoltaic cells, comparing the active junction illumination and current flow directions.

experience shows that these are difficult to achieve in the thin semiconductor films which would almost certainly form the basis for the cell. It is felt that these theoretical considerations, taken with the practical results which have been obtained with these cells, indicate that the chances for developing reasonably high efficiencies in devices using the high-voltage photovoltaic effect are very small, and that re-opening this area of investigation is unlikely to be fruitful.

VI. SUGGESTIONS FOR FUTURE INVESTIGATIONS

VI. SUGGESTIONS FOR FUTURE INVESTIGATIONS

A. INTRODUCTION

In this chapter, suggestions are made for specific research projects which are considered particularly worthwhile, based on the evaluation and analysis of the preceding chapter. These suggestions are based largely on the cost-effectiveness criterion, and this involves an estimation of the progress likely to be achieved in a given field. Issue may be taken with this estimation, as with any estimate, and some readers may consider the views expressed here (and in the previous chapter) as too conservative. However, it should be noted that an effort has been made to be as realistic as possible in the estimates given, and to eliminate any undue optimism.

It should be stressed that the analysis and evaluation of the previous chapter, and the suggestions which are given below, are based on logical methods, involving comparison and extrapolation. Such processes have no means of indicating the areas where unexpected phenomena which can be exploited, will occur. For example, a strictly logical analysis, performed 15 years ago, would probably have indicated that research on CdS as a photovoltaic material was very unlikely to lead to a useful solar cell. The present status of the CdS device work demonstrates clearly the limits of such logical analysis. Future discoveries, just as unanticipated, must be expected, but the solar cell field is believed to be sufficiently mature for the suggestions made in this chapter to be useful, provided this limitation of the analysis is borne in mind.

The organization of this chapter is somewhat different from that of the previously presented material. This has been done to permit comparisons to be made between research with similar goals, and to emphasize the fact that these suggestions are made towards the achievement of specific objectives.

One further point has been considered in making several of these suggestions. Approaches to making better solar cells have on occasion received ardent support from those who have developed them, but have not been generally accepted by others because of doubt about the validity of the results claimed. An attempt has been made to single out those ideas which appear to have sufficient merit to warrant efforts at providing a less partisan evaluation. It is felt that in most instances, such independent testing would not only serve as a check on the results claimed, but would also increase the acceptance of the results when proven useful. Such acceptance is important for making a research expenditure an investment that pays off.

B. IMPROVING EFFICIENCY

The improvement of conversion efficiency is an aim of primary importance in the development of solar cells. The suggestions which are made here are arranged in what is considered to be the order of priority for work in this area. The priority is judged on a consideration of:

1. the effort needed to realize a useful practical result for short-to medium-term projects (2-5 years)
2. the likelihood of achieving a useful end product at all in the case of long-term projects (> 5 years).

1. Silicon Cells

Evaluation of the present performance of single-crystal silicon cells of 12-16 mil thickness has indicated that the improvement in conversion efficiency which theory indicates to be possible, could mainly be realized by increasing the collection efficiency for minority carriers. It has also been shown that the cause of the loss in collection efficiency in the present cells is recombination, and that the divergence between theory and practice for this process apparently arises because non-radiative recombination is occurring to a much greater degree than is theoretically predicted. It is clear the nature of the recombination centers active in silicon is not well understood, nor are methods for their elimination known. It is also possible that this nonradiative recombination is connected with the mechanism giving rise to the presently observed divergence between theory and practice for device I-V characteristics. Shockley and Queisser have proposed that metallic impurities in Si solar cells are the cause of this recombination, and have criticized the use of low-quality silicon as the starting material for solar cell manufacture. Their experimental results in support of this hypothesis are not wholly conclusive, however, and in addition the results of Ralph with cells made of high-purity Si indicate either, that initially-present impurities are not the cause of the difficulty, or, that these impurities are equally present in low and high grade silicon.

Hence it is felt that the improvement of efficiency in the currently standard type of silicon cell can best be achieved by identifying the recombination process occurring in these devices. Unfortunately, this is virtually a recommendation for an investigation of recombination in silicon in general: the lifetimes measured in solar cell material have been as long as those measured in any device using silicon of the same resistivity. The research should aim at answering the following questions:

- a. does the recombination process obey the established theory, or must a new theory be formulated to describe the mechanism involved?
- b. what is the species involved in the recombination (impurity or lattice defect), if any?
- c. how does this species become present in the cell, and can this be avoided?

Such a research program would necessarily combine both experimental and theoretical work. It must be noted, however, that the achievement of diffusion lengths of 100 μm

in solar cell silicon implies a recombination site density of the order of 10^6 cm^{-3} . For a carrier concentration of 10^{15} cm^{-3} , this recombination site density could hence be introduced as an impurity of only 1 part in 10^9 in the diffusion source. It is clear that the detection of such low concentrations of impurities in cells is not likely to be quickly accomplished, so that speedy results will not be expected in this area.

The potential improvement in cell efficiency available from improvement of minority carrier collection efficiency is large, as indicated by the data in Table X: in principle, an efficiency of not too far from the theoretical 18.7% (AMO) should be obtained if the other cell operating parameters (V_{oc} , F) remain at the currently achieved values. Such a large improvement is of course highly improbable; nevertheless, the value of a reasonable gain (to 14% AMO average efficiency, for instance), would justify a considerable effort in this area.

A word of caution should be inserted here, however. Radiation damage degrades cell performance principally by reducing minority carrier lifetime, which is precisely the factor which has been discussed above. Cells with a high efficiency achieved by long minority carrier lifetimes can therefore be expected to be especially sensitive to radiation. Thick shielding could prevent this in some cases, but much of the advantage of the higher efficiency cells would be lost because of the increased array mass. The radiation resistance achieved by lithium doping of the cells may be applicable to higher-efficiency devices: only experimental work in this area can answer this question.

In view of the value of increases in conversion efficiency, this program to improve the performance of silicon solar cells is considered to be particularly worthwhile. It should be stressed, however, that refinement of the present cell type has progressed to the point of diminishing returns. Any improvements possible from this approach will therefore only be obtained if a breakthrough is made in reducing minority carrier recombination site density. This implies that an improved cell may have a structure, or be made using fabrication processes, which are based on principles different from those in use today. A project aimed at producing an improved cell by this approach therefore cannot be regarded as a short-term undertaking. Depending on how rapidly the recombination site species can be identified, the project will probably be a medium- to long-term venture (5-10 years). In the short-term, however, small improvements can be expected from the application of established methods for increasing collection efficiency, and it appears likely that this will provide the most efficient solar cells available up to 1973, and possibly for some years beyond that date.

2. Multiple-Transition Solar Cells

The multiple-transition cell is the only photovoltaic device which has been proposed to date which has a theoretical conversion efficiency appreciably higher than that of conventional cell types. The analysis and evaluation in the previous chapter indicates that some uncertainty exists with respect to the theoretical background and even more

with respect to its realization. However, because it has such a large potential, it is believed that research into this approach is justified.

Since experimental work is so much more costly than theoretical work, and bearing in mind the theoretical uncertainties which exist in this case, it is proposed that initial research be aimed at answering these questions:

- a. Does present recombination theory indicate that the device can indeed work according to the preliminary analysis of Wolf?
- b. Assuming the answer to the above question indicates that the cell is in principle possible, what are the minimum properties required of the intermediate energy levels (capture cross-sections, emission probabilities, densities, etc.,) to provide useful cell operation?
- c. Have such intermediate levels been observed experimentally?

The answers to the latter questions should then be used as a guide to experimental work, which should, of course, only be undertaken if the theoretical prognosis remains favorable. The experimental work would have the following objectives:

- a. identifying a suitable host material/active species combination giving the desired energy level structure, and having the necessary semiconduction and optical interaction parameters.
- b. developing methods for fabricating cells.

This experimental work is expected to be both expensive (1-10 million dollars or larger) and time-consuming (5-10 years) if practical devices are to be achieved. (These estimates are based on the experience with the GaAs single-crystal cell development work.) However, the theoretical program proposed as a prelude need not be comparable in cost: \$100,000 to \$200,000 spent in a 1 to 2 year period should be roughly the level of effort needed to examine the questions posed within the limits of the present theory and to augment it with some basic material experiments.

At the time of this writing, the multiple-transition solar cell is believed to be the only device which has the potential of significantly surpassing the silicon solar cell in terms of absolute conversion efficiency.

3. Cadmium Sulfide Thin-Film Cells

For use on normal space missions (i.e., those not involving extremes of temperature or radiation), the most serious near term competitor to single-crystal silicon solar cells appears to be CdS thin-film cells. However, the efficiency of these is at the moment marginal for space applications, and it is highly desirable that this aspect of their performance be improved.

Experimental cells have been made with efficiencies considerably higher than those of the present pilot-line cells. It appears that there was a fundamental difference in processing between the highly efficient cells and those prepared on the pilot-line. This processing method has not been used on the pilot line because obtaining controlled and reproducible results proved more difficult than with the processes presently in use. It appears desirable that this lead be followed up, and that the high-efficiency processing method be investigated further.

The theoretical efficiency of the cell, as calculated from the tentative model described in Section V-E above indicates that both V_{oc} and J_{sc} can be improved by roughly equal amounts (see Table XII), but that F can potentially not be much increased. To improve V_{oc} and J_{sc} , and to provide a more accurate evaluation of the increases potentially available, work aimed at improving the present understanding, and hence the theory, of CdS cell operation is highly desirable. Such work is presently in progress at Clevite Laboratories, and is believed to be of great potential value. Since the phenomena seen in CdS cells are strongly dependent on the processing involved in their manufacture, it appears to be essential that analytical work of this type proceed as closely as possible in conjunction with a production facility, so that the theoretical results will correspond closely to real cells. Again, the Clevite work meets this criterion.

This investigation of the cell mechanism ideally would answer the following questions:

- a. what is the band structure of the cell?
- b. to what I-V characteristic does this band structure lead?
- c. what collection efficiency can be expected from this band structure?
- d. how can the manufacturing process be altered so as to give a band structure leading to higher efficiencies?
- e. what is the carrier generation mechanism?
- f. what is the collection mechanism?

The Clevite work has gone a good way towards answering question a., and it is hoped that answers to the remaining questions will be obtained in the near future.

4. Cadmium Telluride Thin-Film Cells

For the present CdTe cells, an efficiency improvement appears to be vital if application of these cells is to be achieved. In contrast with the CdS cells, the mechanism and theoretical understanding of this cell is well developed. Hence, the data displayed

in Table XII is taken to reflect the potential improvement fairly accurately. This shows that it should be possible to obtain increases in all the operating parameters, V_{oc} , J_{sc} and F . Investigation of alternative processing methods to improve these factors appears to be necessary, and the effort expended on this device in the near future should be shifted from pilot line operation to obtain quantities of cells towards achieving more efficient cells. One area which should be pursued in pilot line operation, is the improvement of the CdTe layer deposition process, to give more uniform material. Such work is already in progress, and a successful outcome of this endeavor could do much to close the rather large gap which at present exists between the efficiencies of pilot-line and laboratory cells.

5. Gallium Arsenide Cells

To improve the performance of single-crystal GaAs cells, the analysis in the previous chapter shows that the major factor capable of being improved is J_{sc} , since V_{oc} of F are already near their ideal values. It appears that the same type of research program as is proposed for improving J_{sc} in silicon cells, would be applicable to GaAs cells too. There is one point of difference, however, in that the minority carrier collection occurs principally from the base region of the silicon cells, whereas in the GaAs cell, a major contribution to J_{sc} occurs by collection of minority carriers generated in the diffused surface region. Because of the small thickness of this region, and the gradient of impurities existing in it, arising from the diffusion process, research into the recombination mechanisms in the GaAs cell is likely to be more difficult than in the Si cell. In addition, it is felt that implementing any proposals made for ways to improve GaAs cells is likely to be difficult because of the incompletely developed technology available for this material.

Thin-film GaAs cells would need to be improved very considerably in efficiency before they could be seriously considered for application. GaAs is potentially an excellent material for such cells, but the growth processes available for forming thin films in the past led to a material quality which seriously limited the cell efficiency. Any future work on thin-film GaAs cells must start by developing new methods for making the base material.

Although improvements in the conversion efficiencies of GaAs cells are clearly possible, it is believed that the effort needed to achieve such results would be very large. Hence, work in this area is considered to have a low priority.

C. IMPROVING POWER-TO-WEIGHT RATIO

The evaluation of the work on silicon cells and thin-film cells has indicated that there are at present two primary candidates for satisfying the needs of future high power arrays — the thin silicon cell and the thin-film cadmium sulfide cell. The

thin-film cadmium telluride cell has been found to be somewhat less promising at its present stage of development. The question of whether the thin silicon cell or the cadmium sulfide cell will ultimately prove superior cannot be decisively answered at present because of a lack of understanding of the basic limitations of the cadmium sulfide cells. On the basis of the presently available evidence it is felt that the thin silicon cells will probably prove to be the more acceptable from the point of view of offering the best combination of power per unit weight, power per unit area, and reliability. Consequently, the first general recommendation in the area of improving cell power-to-weight ratio is that interest in the development of thin silicon cells should be increased.

1. Thin Silicon Cells

The following specific suggestions are offered as areas which might profitably be investigated, or in which the continuation of work is desirable, for the improvement of thin silicon cells.

- a. The cause of the anomalous behavior of the short circuit current of the thin cells, as discovered by Wolf and Ralph, must be determined and eliminated. The work of Crabb and Treble, and Burrill et al, discussed in the evaluation section of this report, indicates that the problem may be associated with defects introduced by cell processing, and that solutions may be obtained by the proper introduction of impurities. This work provides a basis for further investigations in this area.
- b. The finding of Cheslow and Kaye that the short circuit currents of their 0.004" thick drift field cells were larger than those of their 0.004" thick field free cells should be further investigated. Initial steps in this direction would consist of a theoretical analysis to determine how much of an effect, in principle, the inclusion of a drift field will have on the performance of thin cells and what type of field configuration would be desirable to optimize performance. Cheslow and Kaye have provided an estimate of the effect for the specific case of the 0.004" thick cell in their analysis, which indicates that an improvement of approximately 20% in collection efficiency could result. This analysis assumes a constant field and mobility throughout the drift field region and small signal operation. An analysis including a variable field and mobility as well as various cell thicknesses would be desirable. This information could be obtained by a slight modification of existing analyses. An experimental program incorporating drift fields in thin silicon cells should be initiated if the results of a more thorough analysis confirm those obtained by Cheslow and Kaye. It must be remembered that introducing a drift field involves additional process steps and thus costs.

- c. Information on the effects of reflecting back contacts on the sunlight operation of thin silicon cells is needed. Burrill et al have published data showing appreciable improvement in cells when reflecting contacts are used. Their use of tungsten illumination in these measurements, unless supplemented by sunlight calibration for each individual cell, would considerably distort the characteristics of these cells with reference to actual operating conditions. The effects of these contacts on the effective minority carrier lifetime in the base region of the cell also require further study.

2. Cadmium Sulfide Cells

The cadmium sulfide thin-film cell has long been realized to offer potential advantages over presently used cells from a power-to-weight ratio standpoint. This has been one of the reasons for the considerable investment made by government and private industry in the development of these cells. As a result of this work, cells having power densities above 100 watts per pound have been produced. Further advances in this area are continually sought. One of the important ways in which the power-to-weight ratio of the present cells can be increased is by improving their efficiency. Discussions of this approach appear in the preceding section. No fundamentally new suggestions for decreasing the weight of the cadmium sulfide cells can be given. The best that can be done is to suggest that work along present lines be continued and to list those areas of investigation which might be emphasized to improve the power to weight ratio. Only areas offering significant potential for weight reduction are discussed here.

The cadmium sulfide layer and the Pyre M.L. conductive varnish are the largest single contributors to the weight of the cell, constituting approximately 37% and 26%, respectively, of the total. The cadmium sulfide layer on present cells is about 20 μm thick. Cells were made by National Cash Register on cadmium sulfide layers which are only 1-2 μm thick, although they were not really good cells (efficiencies of $\sim 3\%$). The NCR group used a spraying technique to deposit their barrier layers rather than the solution dip process employed by most other groups. Barriers formed by the dipping process may give rise to more shorting due to diffusion down the grain boundaries. The possibility that the crystal structure of the sprayed CdS films may be better (or worse) than that of the evaporated films at thicknesses approaching 1 μm can also not be neglected. The thickness of the CdS layer on the thin film cells has gradually been decreasing over the years and a continuation of this trend is desirable. Similarly, reductions in the thickness of the conducting varnish can probably be tolerated and would significantly reduce cell weight; otherwise, replacement by higher conductivity layers may be indicated.

Another area in which success will lead to a weight reduction is the development of a viable vacuum deposition or plating process for grid formation. Work on such a technique has been pointed out as being desirable for a number of other reasons also. The

present electroformed mesh grid constitutes only about 10% of the total weight of the cell so that gains in this region will not be large, however, a small reduction in grid weight can be realized because grids formed by the above two techniques will not need cross bars for support as does the electroformed grid. Computations indicate that the thickness of the grids must be comparable to those of the present mesh for efficient operation, so that weight reduction through the use of thinner grids is not feasible with the present cell geometry.

3. Cadmium Telluride Cells

The cadmium telluride thin-film cells are felt not to be competitive with other light weight cells at the present stage of development because of low efficiencies in pilot line production, and relatively high weight when the molybdenum substrate is used. Recent efforts to make use of thin aluminum foil as a substrate material may lead to alleviation of the second problem. The ultimate solution to improving the power-to-weight ratio of the cadmium telluride cell would be the development of a plastic capable of withstanding temperatures of 400-500°C.

D. REDUCING ARRAY COST

As arrays get larger in response to heavy power demands it becomes increasingly important to reduce the cost per unit power output of the array. There are two regions within the sphere of array cost which are relevant to this discussion of photovoltaic cells: the cost of manufacturing the cells and the cost of assembling and connecting the cells into an array. Other areas will not be treated. In general it can be stated that more application of automated techniques will be needed if future space missions require huge quantities of solar cells. A number of the processes involved in silicon cell manufacture have not been amenable to automation in the past. Solutions to these problems could become a necessity in the future, if much larger quantity production should be required.

1. Cell Cost

One way to help in reducing both cell and array manufacturing cost (i. e., cost per unit power) is to increase cell area. The resulting savings in handling cost can be considerable, especially in the array assembly area. Both thin-film and silicon cell technologists have been responsive to this fact and have attempted, with varying degrees of success, to produce large area cells. The thin-film cell work has been highly successful along this line and recent information indicates that they may be cost competitive with present silicon cells, despite their relatively poor efficiency. Of the various techniques for producing large area single crystal sheets of silicon, the dendritic growth technique appears to be the only one having a reasonable prospect of yielding a practical lower cost process in the near future. The following suggestions for decreasing cell cost are not new, but it may be interesting to see them summarized.

- a. In the area of thin-film cells, it is felt that realization of the ultimate in cost savings hinges on the development of a capability for complete cell processing in a single environment, thereby allowing automated fabrication. There are two techniques worthy of consideration. The first is the all vacuum approach, which is an extension of the present thin-film cell technology. The major problems which prevent the present technology from evolving into an all vacuum technology is the lack of the process for successfully depositing barrier layer and grid contacts in vacuum.

The second possible approach is the all air or gaseous environment approach. Present barrier formation techniques are compatible with such a technique. Development work on the formation of a suitable semiconducting layer (CdS) and the deposition of grid lines is necessary for this approach. For the deposition of the semiconductor layer, the screen deposition and sintering technique used by RCA in photoconductor manufacture, and the spray technique of National Cash Register and RCA suggest themselves.

- b. The silicon dendritic cell approach needs additional work on the control of the dendritic growth process so that material of uniformly good quality can be obtained, and on cost reduction for the process. Present irregularities and poor quality not only appear to affect cell yields, but also to contribute to handling problems which necessitate cost special processing. If the growth process cannot be brought under better control, low-cost dendritic cells may not be realized.

2. Array Assembly Cost

The assembly of extremely large arrays of solar cells could benefit from the development of automated or semi-automated mounting techniques to keep cost and assembly time within reasonable limits. Repeated attempts in this direction have been undertaken in the last 10 years, but general exploration of the possibilities in this realm is not within the scope of this discussion. One suggestion, however, is that a considerable proportion of the assembly effort could be eliminated if cells could be produced in the form of integrated submodules. The above mentioned semi-automated thin film sub-module production would be ideal for this. With the proper masks, arrays of series and/or parallel-connected cells could be produced in one continuous process. Unfortunately, processes for continuous fabrication of cells are not presently known. However, integrated arrays could be fabricated by present techniques at costs which should be comparable to present silicon cell cost. Savings in array assembly costs might thus be realized. It is suggested, then, that development of techniques for fabricating arrays or sub-modules, consisting of a number of interconnected cells on a single substrate, should be undertaken.

E. REDUCING CELL DEGRADATION

1. Silicon Cells

At present, the approach which appears to offer the most promise of achieving higher radiation resistance in single-crystal silicon solar cells is by the use of lithium doping. Work aimed at elucidating the mechanisms which give rise to the observed phenomena is believed to be of particular importance if confidence in the application of these devices is to be established. This is an area which is being actively investigated at the present time, and it is hoped that the present rate of progress can be maintained.

More conventional approaches to minimizing the effect of radiation damage, as by using the n/p configuration with junction depth minimized to increase the blue response, are still worthwhile. The evaluation of this area of research, described in V-C above, indicates that improvement in radiation resistance can in principle be obtained by making cells with shallower junctions, and hence it is proposed that further work be done towards applying and further developing the methods outlined by Mandelkorn for making junctions appreciably shallower than in the present commercial cells, and for fabricating suitable contacts to these cells.

These objectives could be met by a modest, short-term development effort (\$50,000-\$100,000) over a half to one year period to be followed by production methods development. The potential applicability of this approach in all silicon cells makes the effort well justified.

The comparative radiation resistance of the thin (4 mil base) cell compared to the normal silicon cell is inherent in the device geometry, for the reasons discussed in the previous chapter. The effect of adding a drift field to improve the efficiency of the thin cell should provide an additional improvement in radiation resistance: this is also discussed in the previous chapter. Thus the proposed program of work aimed at bringing 4-mil thickness drift-field cells into general use because of power-to-weight ratio and conversion efficiency advantages, will lead to a comparatively radiation-resistant cell.

Another degradation problem in silicon solar cells has recently been found. Although little is yet known about this problem, it is characterized by a loss in conversion efficiency of arrays assembled from solderless cells (i.e., cells with Ag-Ti evaporated contacts, but not solder-dipped) with cover-glasses attached with silicone rubber adhesive. Since solderless cells have a demonstrable advantage in saving weight, it is desirable that work be initiated to identify the mechanism giving rise to the observed phenomenon, and to develop methods for preventing the degradation. This would appear to be a short- to medium-term problem, and there appears to be no reason to believe that elimination of the problem cannot be achieved within 2 to 3 years.

2. Thin-Film Cells

In principle, the same situation as for 4-mil silicon cells exists for thin-film cells, but to an even larger degree. Because the active region of thin-film cells is very narrow, the devices are inherently resistant to particle irradiation. As these cells approach application, engineering data on their behavior under irradiation will of course be needed, and in particular, the radiation effects on the encapsulation materials will have to be investigated. Such work has been done on a piece-meal basis in the past, and no special problems have been noted.

The plastic-encapsulated thin-film CdS cells can only be made resistant to UV radiation at the present time by encapsulation with Kapton, which, however, absorbs photons in the spectral sensitivity range of the cell. It is proposed that a search be initiated specifically aimed at finding a plastic film which combines the required optical transmission with UV radiation resistance and suitable mechanical properties. Searches of this type have been performed in the past by those involved in the cell development, but a direct project at one of the laboratories engaged in plastics research, might be more likely to be successful in this direction.

The degradation in performance of CdS thin-film cells on storage and on temperature cycling is likely to prove a far tougher proposition. It has been asserted that the newest method of cell fabrication has solved this problem, and it appears that a portion of the recent cells are reasonably stable provided the temperature cycling does not exceed the range of -100 to $+60^{\circ}\text{C}$. However, this is not unequivocally true for all cells, so that a sustained testing program to provide a continuous analysis of the uniformity and stability of pilot line production cells is required. The testing performed at NASA-Lewis and at Boeing, as reported by Spakowski, and at Lincoln Laboratory, appears to be a sound approach to providing the needed information, and it is urged that such programs be continued.

The solution of the stability problem, however, inevitably falls upon the cell manufacturers. An understanding of the mechanisms leading to the degradation will be needed, as evidenced by the present work of the Clevite group. It is urged that this work be pursued vigorously.

Evaluation of the work on the CdTe thin-film cells' stability indicates that work aimed at solving the humidity degradation problem is urgently needed. This is being tackled at the present time by an evaluation of various encapsulating methods to prevent moisture penetration into the active region. In the absence of an alternative approach, this work should be continued. The combination of this search with that proposed for the CdS UV-resistant encapsulant could prove beneficial, and should minimize duplication of effort.

3. Organic Materials

In the evaluation and analysis of work on cells based on organic materials, it was proposed that future work in this area be guided by the results of radiation damage studies. Accordingly, it is suggested that, in the immediate future, such studies be the only work in the field of organic semiconductors. The following objectives should be included in such a research program:

- a. . to examine the effect of particle and UV irradiation on specimens of photo-sensitive organic compounds.
- b. to determine whether or not general rules can be formulated to predict the behavior under irradiation of a compound containing given radicals and structural bonds.
- c. to provide recommendations to guide in the choice of candidate compounds for use in organic photovoltaic cells.

The necessary information may in fact be obtainable from published studies of radiation chemistry not specifically related to photosensitive materials. Even if experimental work is required, however, it appears that the initial premise on which this suggestion is based can be proven or refuted by a short-term (1 year) low-budget (\$100,000) effort, and the needed information can be assembled by continuance of the same level of effort, should the concept prove useful.

**APPENDIX I. AN APPROXIMATE ANALYTICAL
EXPRESSION FOR FILL FACTOR**

GLOSSARY OF SYMBOLS FOR APPENDIX I

A	empirical constant in the diode equation
B	J_L/J_o
C	composite parameter introduced for convenience and defined in the text
F	fill-factor
F'	approximate fill-factor
J	current density
J_D	diode current density
J_L	light-generated current density
J_{mp}	maximum-power-point current density
J'_{mp}	approximate maximum-power-point current density
J_o	reverse saturation current density
J_{sc}	short-circuit current density
k	Boltzmann's constant
P	power
q	electronic charge
R_s	series resistance
T	absolute temperature
V	voltage
V_{mp}	maximum-power-point voltage
V'_{mp}	approximate maximum-power-point voltage
V_{oc}	open-circuit voltage

APPENDIX I

AN APPROXIMATE ANALYTICAL EXPRESSION FOR FILL FACTOR

1. Statement of the Problem

It is experimentally convenient to state the performance of a solar cell in terms of V_{OC} , J_{SC} , and F . The V_{OC} and J_{SC} can be easily related to theoretical treatments, but this is not true for F , since there is no explicit expression giving this in terms of other cell parameters such as J_L , R_s and J_0 . This arises because the equations which must be solved to obtain the maximum power point in terms of the cell parameters are transcendental, and can only be solved numerically or graphically. Although this is a straightforward problem, it is time-consuming and inconvenient, and it would frequently be useful to employ an explicit expression giving approximate V_{mp} , J_{mp} , and F values. The derivation of suitable expressions is described below.

2. Derivation of a Solution

The equivalent circuit of the solar cell which will be analyzed is as shown in Figure 95. Shunt conductance across the cell output is not accounted for, since this has negligible effects in experimental solar cells of good quality. The I-V characteristic of the diode is taken to be:

$$J_D = J_0 \left(\exp \frac{qV}{AkT} - 1 \right) \quad (134)$$

This leads to the cell having the I-V characteristic:

$$J = J_0 \left(\exp \frac{q}{AkT} (V - JR_s) - 1 \right) - J_L \quad (135)$$

The power generation density in the cell is

$$P = V \times J \quad (136)$$

and by combining equations (135) and (136) P can be expressed in terms of either V or J alone. P can then be maximized by finding the stationary points by the usual techniques, which unfortunately lead to transcendental equations in this case. Inspection of the I-V curve for a solar cell shows that it is very similar in shape to a rectangular hyperbola, in the power generation region. This suggests that an approximate maximum power point can be obtained by determining the point at which a tangent to the

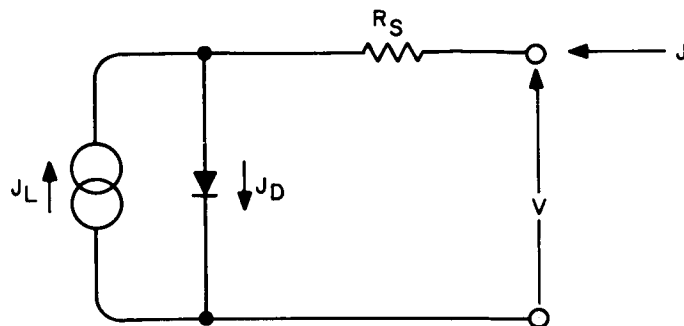


Figure 95. Simplified equivalent circuit of a solar cell.

I-V curve is parallel to a straight line through the V_{oc} and J_{sc} points, i.e., the point at which:

$$\frac{dV}{dJ} = \frac{V_{oc}}{J_{sc}} \quad (137)$$

Using this assumption, approximate maximum power point parameters are derived:

$$V'_{mp} = \frac{AkT}{q} \ln\left(\frac{B}{C}\right) + J_L R_s \left(\frac{1}{C} - 1\right) \quad (138)$$

$$J'_{mp} = J_L \left(\frac{1}{C} - 1\right) \quad (139)$$

where

$$B = J_L / J_o$$

$$C = \ln B - \frac{J_L R_s q}{AkT}$$

It is assumed that:

$$J_L \gg J_o.$$

(Primed variables are used to represent approximations derived by this procedure.)

Since

$$F = \frac{V_{mp} \times J_{mp}}{V_{oc} \times J_{sc}}$$

it can be easily shown from (138) and (139) above that:

$$F' = \left[\ln B - \ln C + \frac{J_L R_s q}{A k T} \left(\frac{1}{C} - 1 \right) \right] \times \left[1 - \frac{1}{C} \right] / \ln B$$

For the ideal cell, where $R_s = 0$, these expressions can be simplified:

$$V'_{mp} = \frac{A k T}{q} \ln \left(\frac{B}{\ln B} \right) \quad (140)$$

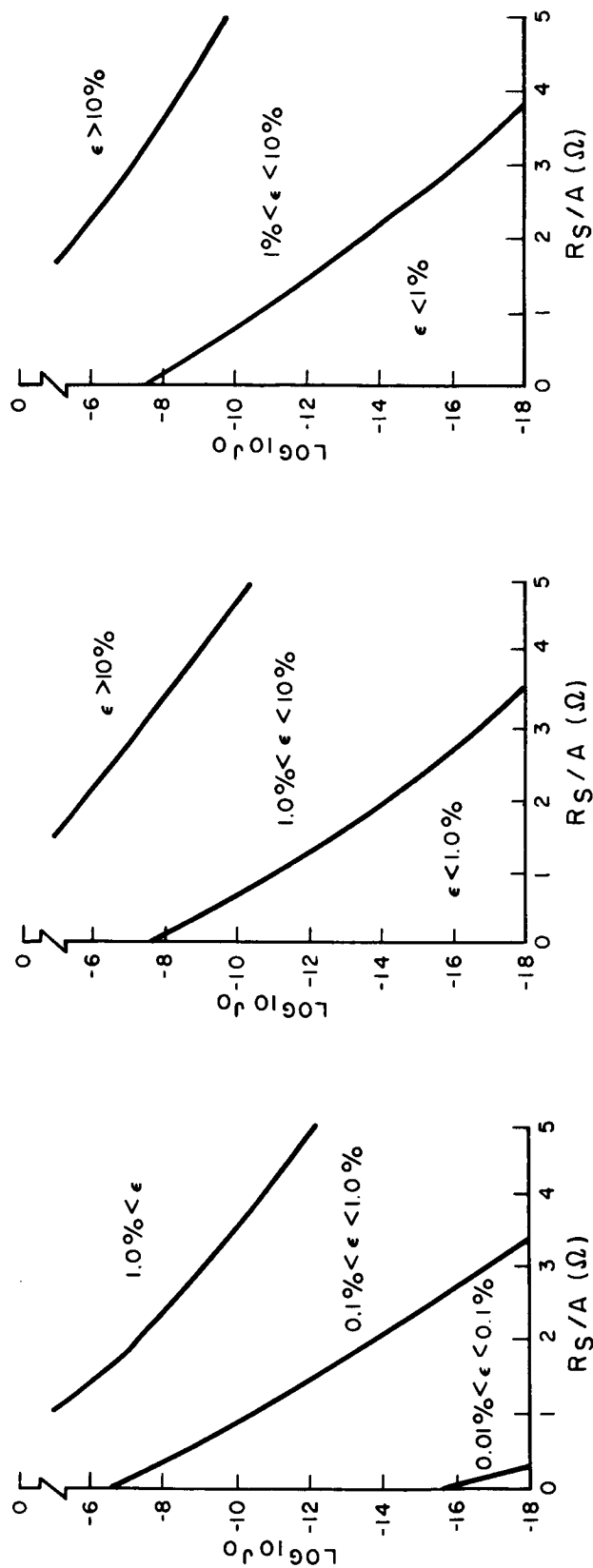
$$J'_{mp} = J_o \left(\frac{B}{\ln B} \right) - J_L \quad (141)$$

$$F' = \frac{(\ln B - \ln \ln B) (\ln B - 1)}{(\ln B)^2} \quad (142)$$

3. Comparison Between Theory and Practice

To provide some guide to the accuracy of these approximations, the results from their use have been compared with the accurately determined V_{mp} , J_{mp} , and F values from precise numerical solutions. The results are displayed in Figure 96, which show the domains within which various accuracies are obtained as R_s , J_o , and A change. The value of J_L was taken as $40 \text{ mA} \cdot \text{cm}^{-2}$ for these calculations. Inspection of equation (135) shows that for ($J_L \gg J_o$) the curve shape will be invariant under changes of the parameters R_s and A , provided the parameter (R_s/A) remains constant, although a scaling factor change in V will be produced. The invariance of the curve shape, however, results in the errors for the maximum power point parameters being the same at a given value of J_o and (R_s/A), so that these have been used in plotting Figure 96.

The results show that the approximation leads to errors less than 1% in F for most practical cells of good efficiency, but that errors between 1 and 10% will generally exist in the V'_{mp} and J'_{mp} values. The approximation always gives F' values smaller than the true F' , as would be expected. Also, $J'_{mp} > J_{mp}$, and $V'_{mp} < V_{mp}$ in all cases.



a. Accuracy of approximation for F b. Accuracy of approximation for V_{mp} c. Accuracy of approximation for J_{mp}

Figure 96. Charts showing the results of various accuracies of approximation for a cell with given values of J_0 and R_S/A

APPENDIX II. OPTIMIZATION OF GRID STRUCTURES

GLOSSARY OF SYMBOLS FOR APPENDIX II

A	cell area
I_L	light-generated current
I_{mp}	maximum-power-point current
J_{mp}	maximum-power-point current density
L	cell length
M N	{ composite parameters introduced for convenience and defined in the text
P	power delivered to load by cell
R_S	cell series resistance
S	grid aperture width
T	grid line width
V_{mp}	maximum-power-point voltage
W	cell width
ρ_S	sheet resistance of diffused region
ρ_T	sheet resistance of grid line

(For a graphical definition of L , S , T , and W , see Figure 36.)

APPENDIX II

OPTIMIZATION OF GRID STRUCTURES

1. Statement of the Problem

Consider a cell with the usual contact comb structure as shown in Figure 36. (The nomenclature follows that of Wolf, reference 194.) Series resistance in the device arises from contributions from the resistance of the grid line, and from the surface resistance of the diffused region. Application of more grid lines, and increasing their width, reduce the series resistance, but cause a loss in I_{SC} for the cell, by obscuring the active region. A trade-off analysis will be performed, to derive expressions allowing the optimum grid geometry to be calculated in terms of the various cell parameters.

In the usual case, the overall dimensions of the cell are determined by manufacturing convenience or application suitability considerations, thus fixing W and L for the device. It remains to choose suitable values of T and S to maximize the power output. We assume that the geometry of the contact strip is fixed by contacting reliability or manufacturing considerations, as is normally the case, and for ease of analysis, the current collection directly onto this contact is neglected. Some comments on these points are in order:

- a. If the resistance of the contact strip is neglected, the efficiency of the cell is independent of L .
- b. The efficiency of the cell increases monotonically as W is reduced, if the contact strip is regarded as being external to the cell proper.
- c. It can be shown that neglecting current collection directly onto the contact strip is equivalent to assuming that:

$$\frac{\rho_s S}{8W} + \frac{\rho_T W}{2T} \ll \frac{\rho_s W}{2S} \quad (143)$$

For the values of ρ_s , ρ_T , and T in most cells, this is equivalent to assuming that

$$W \gg S \quad (144)$$

2. Choice of T

A condition for optimum T does not exist, or rather, would lead to $T \rightarrow 0$. This can be quickly shown by reductio ad absurdum of the assumption that an optimum value of T existed.

Suppose an analysis has indicated that for a cell with given W and L, the "optimum" grid has geometry S and T. Then the contribution from the diffused layer and the grid lines to the cell series resistance is given by:

$$R_s = \left(\frac{\rho_T W}{2T} + \frac{\rho_s S}{8W} \right) \times \frac{(S+T)}{L} \quad (145)$$

This follows the analysis of Wolf (194), and assumes that the effect of the distributed resistance on the cell characteristics can be approximated with good accuracy by a lumped R_s , as in the equivalent circuit of Figure 95. This is a good approximation for reasonably efficient solar cells, where R_s is low.

Consider now a cell with the same W, L, ρ_s , and ρ_T , but with $S' = S/2$ and $T' = T/2$. I_L (and hence I_{sc} in a cell with low R_s) will be the same in the two cells, but the series resistance contribution in the second cell, R'_s is given by:

$$R'_s = \left(\frac{\rho_T W}{2T} + \frac{\rho_s S}{32W} \right) \times \frac{(S+T)}{L} \quad (146)$$

Thus the contribution from the grid lines remains the same, but that of the diffused region has decreased by a factor of 4, and the new cell has a resistance lower than that of the cell with the "optimum" grid geometry.

Hence R_s can be reduced monotonically by making S and T smaller (provided ρ_T remains the same, which in practice may not always be true). It follows that in the practical case, T should be made as small as technology will allow, and it remains only to calculate the optimum value of S to be used with a given value of T and the other device parameters.

3. Optimization of S

Ideally, the power available from a cell with a given value of S would be maximized by expressing P as a function of S, and using standard calculus techniques. In practice, this leads through rather complex algebra to a non-analytic solution. For use in most real situations, approximations can be made which lead to a more tractable analysis and to equations which can be solved more easily.

It is assumed that the power available from a cell with a small value of R_s is given by:

$$P = V_{mp} \times I_{mp} - I_{mp}^2 \times R_s \quad (147)$$

where V_{mp} , I_{mp} are the maximum-power-point parameters where $R_s = 0$ for the cell. This assumes that I_{mp} for the cell is the same both with and without R_s present, which is patently untrue. However, for small values of R_s , P is not greatly sensitive to changes in I close to the maximum power point, because of the shape of the I-V curve. The assumption is also equivalent to stating that, in Figure 97, the area of the region (ABCFED) is equal to that of the region (BCHG). This approximation is sufficiently close for most practical situations, but it should be borne in mind that it provides a limitation on the applicability of the results which follow.

It is required to maximize the power per unit area generated by the cell, by varying S .

$$\begin{aligned} \text{Power per unit area} &= \frac{P}{A} = \left[I_{mp} \times V_{mp} - (I_{mp})^2 \times R_s \right] / A \\ &= \frac{J_{mp} V_{mp} S}{S+T} - \frac{(J_{mp} WS)^2}{(S+T)W} \left(\frac{\rho_T W}{2T} + \frac{\rho_s S}{8W} \right) \end{aligned} \quad (148)$$

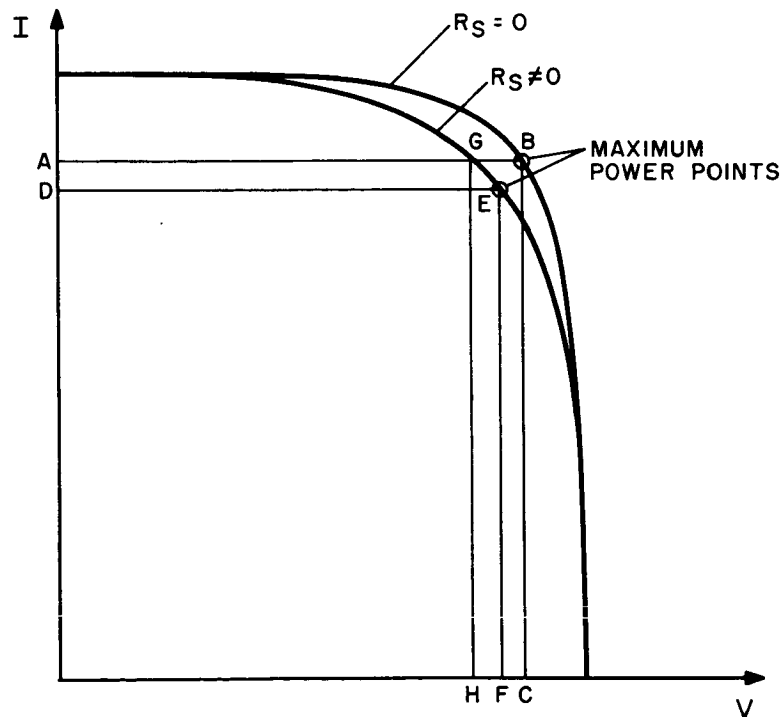


Figure 97. I-V curves for solar cells with and without series resistance, showing effect of approximation used in optimum grid spacing analysis.

Putting $d(P/A)/dS = 0$ to obtain the stationary points, gives (with some manipulation):

$$S^3 + \left(\frac{2W^2}{T} \cdot \frac{\rho_T}{\rho_s} + \frac{3T}{2} \right) S^2 + \left(4W^2 \cdot \frac{\rho_T}{\rho_s} \right) S - \frac{4VT}{\rho_s J_{mp}} = 0 \quad (149)$$

where it is assumed that the reverse saturation current density is given by only the cell area not covered by the grid lines; this will introduce a very small error compared with the assumption discussed above.

It can be shown that this equation has one positive real root (the required value), and two negative roots with no practical significance. Although standard algebraic techniques can be applied to obtaining analytically the required root of equation (149) it is in practice less effort to solve the equation using graphical or numerical methods.

Finally, we note that if:

$$\rho_T \ll \rho_s \left(\frac{ST}{4W^2} \right)$$

the grid line resistance can be neglected. In this case, the algebraic methods for obtaining the root of the cubic equation give comparatively tractable results:

$$S = M + N - T/2 \quad (150)$$

where

$$\begin{matrix} M \\ N \end{matrix} = \left[\frac{2V_{mp} T}{\rho_s J_{mp}} - \frac{T^3}{8} \pm \sqrt{\frac{V_{mp} T}{\rho_s J_{mp}} \left(\frac{4V_{mp} T}{\rho_s J_{mp}} - \frac{T^3}{2} \right)} \right]^{1/3} \quad (151)$$

In many cases:

$$\frac{V_{mp} T}{\rho_s J_{mp}} \gg \frac{T^3}{2}$$

and the solution reduces to:

$$S = \left(\frac{4V_{mp} T}{\rho_s J_{mp}} \right)^{1/3} \quad (152)$$

if $S \gg T$ (as is normal).

It is interesting to apply these results to present-day cells, to compare the calculated optimum grid spacing with that determined experimentally. Three cases will be considered:

- A 2 x 2 cm solder-dipped silicon cell, with the grid line cross-section as shown in Figure 98. The minimum technologically possible grid line width is taken as 5 mils, and the silver-titanium layer is electrically in parallel with the solder fillet, giving $\rho_T = 10^{-2} \Omega \cdot \square^{-1}$.
- A 2 x 2 cm solderless cell with a structure identical to (a) except that ρ_T is raised by omission of the solder fillet.
- A 55 cm² CdS thin-film cell, in which it is assumed that electrical conduction in the grid bars running normal to the major direction of current flow can be neglected.

The needed cell parameters for each case have been taken from the literature, and are displayed in Table XV, together with the results of the calculation for optimum S, and the empirically determined optimum S values. For each of these cases, the "negligible ρ_T approximation" could not be used, and it was necessary to solve equation (149) accurately.

It is seen that the agreement between the analysis and the experimental results is fair. Considering the broadness of the maximum in the empirical optimization process (it was found that for solder-dipped Si cells, 4, 5, or 6 grid lines gave almost identical results), the agreement must be considered satisfactory.

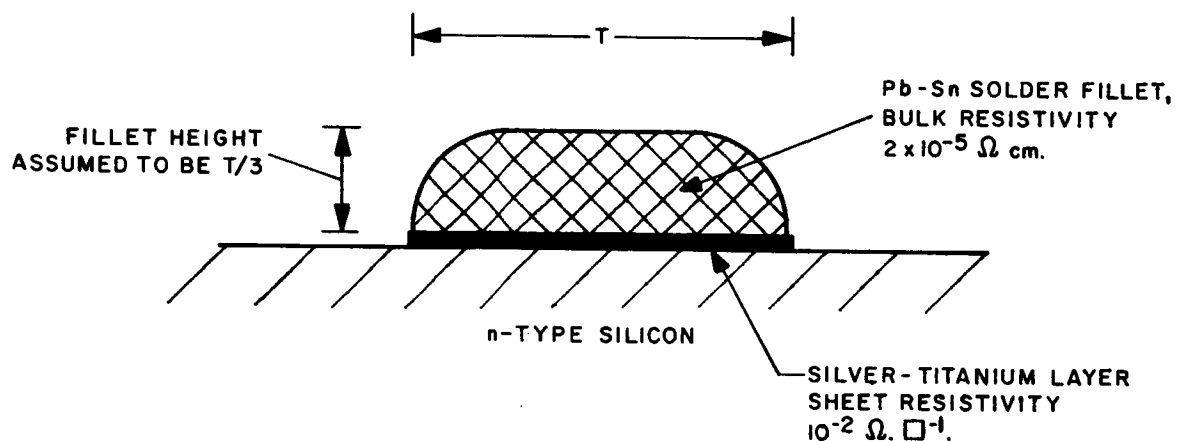


Figure 98. Cross-section through grid line of a solder-dipped silicon cell, showing geometry assumed for sheet resistivity calculation.

TABLE XV. CELL PARAMETERS USED IN OPTIMUM S VALUE CALCULATIONS,
AND RESULTS OF THE ANALYSIS FOR SI SINGLE-CRYSTAL AND
CdS THIN-FILM CELLS.

Cell Type	ρ_T $\Omega \cdot \square^{-1}$	ρ_S $\Omega \cdot \square^{-1}$	T cm	W cm	J_{mp-2} A·cm ⁻²	V_{mp} V	Calculated Optimum S cm	Empirical Optimum S cm
Si, Solder Dipped	3.6×10^{-3}	10	1.25×10^{-2}	2.0	3.6×10^{-2}	0.40	0.319	0.4-0.5
Si, solderless	10^{-2}	10	1.25×10^{-2}	2.0	3.6×10^{-2}	0.40	0.239	0.33
CdS, thin-film	1.35×10^{-2}	10^3	6.3×10^{-3}	7.4	2.0×10^{-2}	0.40	4.31×10^{-2}	3.98×10^{-2}

**APPENDIX III. CHRONOLOGY OF GOVERNMENT-AGENCY FUNDED
RESEARCH AND DEVELOPMENT PROJECTS
RELATING TO SOLAR CELLS**

APPENDIX III

CHRONOLOGY OF GOVERNMENT-AGENCY FUNDED RESEARCH AND DEVELOPMENT PROJECTS RELATING TO SOLAR CELLS

The tables given in this appendix summarize the chronology, and the results achieved, for government-supported projects relating to solar cell research and development. The major source for compiling the tables has been the Power Information Center Briefs, but this has been supplemented by independent knowledge to a large degree. All funding level information has been taken from the PIC Briefs, however, so that this is not available for projects not covered by the Briefs. Although every effort has been made to provide as complete a tabulation as possible, the limited sources available make it probable that some projects, particularly from the pre-1960 period, are not included in the tables. In addition, the coverage of the radiation-effects field has been selective rather than exhaustive, since this best matches the needs of the work in hand.

TABLE XVII. SINGLE-CRYSTAL SILICON CELLS (Cont'd)

PIC	Contract Title	Funding Agency	Contractor and Principle Investigator	Program Results	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970
DENDRITIC CELLS (Cont'd)																
-	Investigation of large area dendritic with type germanium photovoltaic cells	USA-EC	Westinghouse (Erick & Merritts)	Developmental work on germanium dendritic thermo-photovoltaic cells.								DA 28-043-AMC-02350(E)				
GENERAL WORK																
701	Investigation of thin sheets of high-quality, single-crystal silicon	USASRD (Mark)	Grace (Fitch)	Attempts to grow Si sheet by float process on lead not successful.	DA36-039-SC-85242 \$84K											
645	High efficiency Si solar cells	USASRD (Hunrath)	Transitron (Berman)	Manufacturing methods for diffused N-P and P-N cells developed to obtain 12% cells cheaply. Good radiation resistance of N-P 'blue' cells noted. High-intensity illumination studied.	DA36-039-SC-85250 \$98K											
746	High efficiency Si solar cells	USAEL (Hunrath)	Heliotek (Ralph)	Multivariable experiments to optimize cell efficiency for normal and high-intensity operation. 70% of production cells > 12% efficient. Polycrystalline cells also examined, 5-13% efficient but best cells on almost single-crystal Si.	DA36-039-SC-90777 \$74K											
-	Pilot line production of high efficiency solar cells	USAF-ASC	Hoffman (Ralph)	Techniques for obtaining high efficiency silicon solar cells were explored, including use of high purity silicon and study of 3 line vs 5 line grid structures. No significant improvement achieved.	AF33(600)-40497											
130	Solar cells	AFORL	Tech. Ops. Inc.	Utilization of unabsorbed photons by antireflection means, optical sensitization in short and long wavelength regions.	AF19(604)-7306 \$40K											
126	Solar cell array optimization	USAF-WP (Massie)	RCA-AED (Reboul)	Cells on glass and plastic substrates delivered, also arrays of 1 sq. ft.	AF33(616)-7415 \$197K											
105	Study & applied research on measurements techniques	USAF-ASD	Hoffman	Test method, spectral tester and standard solar cells developed. Accuracy $\pm 5\%$.	AF33(616)-7946 \$100K											
467 472	Multielement large area solar cell	USASRD	Hoffman	12 sq. in. cells made, 3% cells made. Abandoned for technical reasons.	DA36-039-SC-87426 \$46K											
1243	Solar and thermal energy conversion and storage systems	AFORL (Yannoni)	Tyco Waltham (Rosenberg)	Surface-barrier silicon cells made. No report obtained.					AF19(628)-2845 \$1,150K							
1156	Solar wrap-around cell	NASA-Goddard (Slifer)	RCA Mountaintop (Ling)	Radiation damage to state-of-the-art cells investigated. Wrap-around cells made, modules on p/c substrates fabricated.						NAS5-3812 \$15K						
1036	Experimental investigation of the effects of space environment on solar cell performance	NASA-Ames (Johnston)	Internal	Measurements on cell efficiencies as function of temperature, angle of incidence of illumination, and intensity of illumination, on NP 10 Ω cm Si cells.						NASA Internal						
1260	Silicon solar cell parametric investigations	JPL (Berman)	Internal	Theoretical I-V curves modified to give good agreement with experimental curves for T = 20 - 120°C, illumination intensity 60 - 340 mW cm ⁻² .						JPL Internal						
-	Investigation of a PIN structure photovoltaic cell	USA-EC	MIT-Center for Materials Science and Eng	Theoretical and experimental investigation of properties of thermo-photovoltaic device.								DA28-043-AMC-01978(E)				

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TABLE XVII. SINGLE-CRYSTAL SILICON CELLS (Cont'd)

PIC	Contract Title	Funding Agency	Contractor and Principle Investigator	Program Results	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970
GENERAL WORK (Cont'd)																
1448	High voltage solar cell array segment	AF-APL (Prystaloski)	Westing-house (Bennett)	Prototype hi-voltage (5-cell) unit 7.33% eff. made by diffusion in Si. Cell area 1.974 cm ² .												
1554	Silicon solar cell for high solar spectrum intensities and high temperature.	NASA-Ames (Wilbur)	EOS (Rolik)	Special cell type for use under high-illumination, high-temp. conditions developed. Showed significantly better efficiency than regular cells.												
INTEGRAL COVER-GLASS CELLS																
1155	Integral glass coatings for solar cells	NASA-GSFC (Slifer)	Hoffman (Iles)	Si cells with 2 mil integral cover glass of borosilicate made, 100 cells supplied for testing.												
1368	Optical and electrical properties of silicon oxide	NASA-GSFC (Fang)	Penn. State U. (Vedam)	Growth of oxide layer on cleaned Si surface showed thickness $\propto \log(\text{time})$. Method for measuring SiO/SiO ₂ ratio in oxide layers as function of depth developed, will be used to examine composition of oxide on Si cells.												
1613	Solar cell integral cover glass research and development	NASA-GSFC (Cherry)	Ion Physics (King)	Cells prepared with 1,2,3 mils SiO ₂ on Si showed good thermal shock resistance.												
1690	Development of integrally glassed silicon solar cell	NASA-GSFC (Cherry)	TI (Cole)	SiO ₂ sputtered onto Si cells: withstood thermal shock.												
1715	Integral quartz covered cell panel	USAF-WP (Prystaloski)	Philco	No results to June 67.												

TABLE XVIII. RADIATION STUDIES

PIC	Contract Title	Funding Agency	Contractor and Principle Investigator	Program Results	1960	1961	1962	1963	1964	1965	1966	1967	1968
GENERAL STUDIES													
1151	Solar cell radiation damage studies.	NASA-Goddard (Schach Cherry)	NRL (Brancato)	(i) Annealing of B-doped 10 Ω cm FZ and pulled N/P Si cells studied: some differences seen between behavior after 1 MeV \times 115,30 MeV irradiations. Al-doped cells showed anneal at lower temperature than B-doped cells. (ii) Thin Si cells studied under irradiation. (iii) Integral cover glass cells from 5 manufacturers irradiated and tested: power losses ranged from 4-34% after 5×10^{13} 400 KeV protons.									
-	Radiation effects on silicon solar cells.	NASA	General Atomic (Van Lint)	Defects introduced by 30 MeV electron irradiation identified, and their effects on carrier behavior in Si examined.									

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TABLE XVIII. RADIATION STUDIES (Cont'd)

Pic	Contract Title	Funding Agency	Contractor and Principal Investigator	Program Results	1960	1961	1962	1963	1964	1965	1966	1967	1968
GENERAL STUDIES (Cont'd)													
314	Research on radiation damage to Si solar cells	NASA-GSFC	TRW-Systems (Denney) (Downing)	Studied dependence of radiation damage in photovoltaic devices on type and energy of bombarding particle, and on base material and impurities within it.									
765	Radiation effects on silicon solar cells	NASA-GSFC (Geiger)	General Atomic (Van Lint)	Theory and experiment correlated for introduction rate of defects during bombardment. EPR studies used to identify centers present, and to correlate observed defects with crystal impurities									
817	Webbed dendritic silicon solar cell radiation effects investigation	USAF-APL (Wise)	Westing-house (Babcock)	Attempt to optimize cells for resistance to 2 MeV electrons by considering following parameters: P/N vs N/P; junction depth; base resistivity. Cells were on dendritic material because of anticipated cost savings. Optimum cell was N/P, 10-13 ohm-cm material, junction depth 0.5 micrometers.									
1148	Studies of radiation damage in solid-state materials.	NASA-GSFC (Fang)	University of Illinois (Compton)	B-doped float-zone Si irradiated by Co60. Two levels found at $E_c - 0.3$ eV, $E_v + 0.17$ eV.									
1044	Radiation damage to solar cells.	NASA-Langley (Patterson)	Internal	Commercial Si cells irradiated.									
1150	Electron and X-ray damage in CdS and related materials.	NASA-GSFC (Fang)	University of Delaware (Boer)	Levels in band gap of CdS investigated. Changes in levels after 100-300 keV x-radiation studied. Threshold for radiation damage in CdS 1.5 times higher in vacuum than in air.									
1147	Theoretical investigation of the analysis of radiation damage to solar cells.	NASA-GSFC (Fang)	Catholic U. (Tanaka)	A model giving kinetic equations relating vacancy-interstitial annihilation, vacancy-impurity combination, and vacancy-interstitial production, was found to fit experimental facts, and to be applicable to Li-Si cells.									
-	Research on effects of electron radiation on semiconductor surface properties (subtitled: Effect of low energy electron radiation on silicon solar cells)	USAMC	Brown U. (Santopietro and Loferski)	The effects of electrons with energies too low to produce bulk damage were investigated using a technique involving the comparison of photovoltaic response under strongly and weakly absorbed light. It is found that the output of P/N cells decreases while that of N/P cells increases with flux.									
1169	Radiation effects in semiconductor	USAF-WP (Kulp)	Brown U. (Loferski)	Radiation damage of GaAs-P studied, indicating a lower damage threshold than for GaAs. Radiation damage of ZnS studied by photoconductivity spectral response changes.									
1367	Photovoltaic effects	NASA-GSFC (Fang)	Brown U. (Loferski)	Effect of sub-threshold (115 KeV) electron irradiation on silicon studied. Results showed surface recombination velocity decreased for p-type, increased for n-type Si.									

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TABLE XVIII. RADIATION STUDIES (Cont'd)

Pic	Contract Title	Funding Agency	Contractor and Principle Investigator	Program Results	1960	1961	1962	1963	1964	1965	1966	1967	1968
GENERAL STUDIES (Cont'd)													
1417	Handbook of space radiation effects on solar cell power systems.	NASA-Hq (Smith)	Exotech Inc. (Cooley)	Preparation of new edition of radiation effects handbook.								NASW1345 \$61K	
1687	Hardened solar cell investigation	USAF-WP (McClelland)	Ion Physics (King)	No report received.								AF33-615-67 -C-1158 \$99K	
1716	Effects of ionized particle radiation on solar cells in deep space	JPL (Berman)	Internal	None to April 1967								JPL Internal	
NP CELL DEVELOPMENT													
470	Radiation resistant solar cells	USASRD	Internal (Mandelkorn)	Developed n/p Si cell, investigated dependence of radiation resistance on resistivity of base region, narrow diffused region.		USASRD Internal							
668	Radiation resistant solar cells	USASRD	Internal (Mandelkorn)	Radiation resistance of shallow-diffused NP 13 Ω cm Si cells demonstrated.		USASRD Internal \$25K							
1292	Silicon photovoltaic cell research.	NASA-Lewis (Mandelkorn)	Internal	"Super-blue" cells made and sent for testing on ATS-3. Investigated effect of various impurities on radiation resistance, and emphasized potential exhaustion of Li in annealing process, causing loss of V_{oc} and increase of R_s .									NASA Internal
-	Radiation damage to silicon solar cells.	NASA-GSFC	RCA Labs (Baicker)	Proton, electron, and UV effects on silicon cells examined, damage rates measured. np cells shown to be better than pn.		NAS-457							
465	Investigation of high efficiency photovoltaic energy converters	USASRD (Mandelkorn)	RCA Labs (Wysocki)	Radiation resistance of PN, NP, oxygen-free, oxygen-containing, and various base resistivity cells compared. NP found best. GaAs cells also studied, showed resistance to electrons, but not low energy protons.		DA36-039 SC87417 \$99K							
659	Solar cell radiation damage study	USAF-WP (Carmichael)	Western Elec. (Donnelly)	Radiation resistance of N/P Si, GaAs cells compared. GaAs shown best for proton radiation NP Si best for electron radiation.		AF33(616)-6235 \$49K							
LI/SI CELL DEVELOPMENT													
312	Radiation damage to Si Solar cells	NASA-GSFC (Fang)	RCA-Labs (Wysocki)	Interaction between Li and radiation-induced defects examined for Si, and conditions necessary to make self-annealing cell investigated. Studies on mechanisms involved.								NAS-3788 \$129K	NAS-9131 \$96K
1149	Solar cell radiation damage studies.	NASA-GSFC (Fang)	Internal	Reports and publications on Li-doped cells.								NAS-10239 \$75K	
1366	Solar cell radiation damage studies.	NASA-GSFC (Fang)	RCA (Topier)	Li cells made with efficiencies "comparable to n-on p cells" made, annealing demonstrated. Also single-crystal cells also made.								NAS-9576 \$62K	
1369	Theoretical study of drift field.	NASA-GSFC (Fang)	Princeton R&D (Baicker)	Loss of V_{oc} in Li-Si cells under irradiation seen, similar to effect in drift field cells under irradiation; this thought not inherent to Li-Si cells. Annealing mechanisms being studied.								NAS-9580 \$15K	

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TABLE XVIII. RADIATION STUDIES (Cont'd)

Pic	Contract Title	Funding Agency	Contractor and Principle Investigator	Program Results	1960	1961	1962	1963	1964	1965	1966	1967	1968
Li/Si CELL DEVELOPMENT (Cont'd)													
-	Radiation damage in Lithium doped silicon and silicon solar cells.	NASA-GSFC (Fang)	TRW-Systems (Carter, Downing)	Irradiation testing and diagnostics on Li-Si cells supplied by other manufacturers.								NAS5-10322	
-	Development and fabrication of radiation resistant high efficiency solar cells.	NASA-GSFC (Fang)	Centralab (Iles)	1 x 2 cm Li-doped cells made with process variations to optimize efficiency and radiation resistance.								NAS5-10271	
-	Development and fabrication of radiation resistant high efficiency solar cells.	NASA-GSFC (Fang)	Helotek (Ralph)	1 x 2 cm Li-doped Si cells made with process variations to optimize efficiency and radiation resistance.								NAS5-10272	
-	Development and fabrication of Lithium-diffused silicon solar cells.	NASA-GSFC (Fang)	TI	1 x 2 cm Li-doped Si cells made, some with integral covers. Cell structure and manufacturing investigated by optimization: 12.5% AMI efficiency achieved.								NAS5-10274	
1686	Investigation of Li doped hardened solar cells.	USAF-WP (Massie)	Heliotek (Ralph)	1 x 2 cm Li-doped Si cells made, some with integral glasses and welded contacts. Cell manufacture and construction studied for optimization.								F33-615-67-C-1458	\$150K
DRIFT FIELD CELLS													
685	Improved radiation resistant solar cell	NASA-GSFC (Fang)	EOS (Kaye)	Drift field cells made with epitaxial in Si on p base showed little or no improvement in radiation resistance over 10 μ -cm np cells.			NAS7-92 \$75K		NAS5-3560 \$47K	NAS5-9612 \$41K			
-	Dendritic solar cell and array investigation	USAF-APL (Wise)	Westinghouse (Tarnaja)	Three techniques for forming drift field region explored: 1) diffusion graded base; 2) epitaxially graded base; 3) out-diffused graded base. All formed on dendritic material. Epitaxial gave best results. 11.5% p/N. 11.8% N/P, 17w/lb. Results 1 MeV electrons indicate drift field cells superior. Other energies inconclusive.					AF33(615)-1049				
1364	Drift field solar cell development.	NASA-GSFC (Fang)	Heliotek (Ralph)	Epitaxial p layer on n based used to make drift field. Best cells had 10% efficiency AMO. Radiation damage same or less than for conventional cells.					NAS5-3558 \$52K				
1365	Drift field solar cell development.	NASA-GSFC (Fang)	TI (Bean)	Epitaxial n layer on p base used to make drift field. Best cells had 10% efficiency AMO. Radiation damage same or less than for conventional cells.					NAS5-3559 \$40K	NAS5-9609 \$45K			
1370	Low energy proton irradiation damage of Drift field solar cells.	NASA-GSFC (Fang)	Lockheed De Panglier	Cells used in testing were early experimental types, hence no final conclusion could be drawn.						NAS5-9627 \$30K			

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The contract reports are listed separately from the published papers to permit the latter to be listed by year of publication, while allowing all of the reports on a given contract to be grouped together even when these have not been published in the same year.

In cases of multiple authorship, only the first author's name has been given, for the sake of brevity.

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